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ISSN 2162-5263 (Print)
ISSN 2162-5271 (Online)
DOI:10.17265/2162-5263

Journal of **Environmental Science** and **Engineering B**

Volume 6, Number 8, August 2017



From Knowledge to Wisdom

Journal of Environmental Science and Engineering B

Volume 6, Number 8, August 2017 (Serial Number 62)



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Publication Information:

Journal of Environmental Science and Engineering B (formerly parts of *Journal of Environmental Science and Engineering* ISSN 1934-8932, USA) is published monthly in hard copy (ISSN 2162-5263) and online (ISSN 2162-5271) by David Publishing Company located at 616 Corporate Way, Suite 2-4876, Valley Cottage, NY 10989, USA.

Aims and Scope:

Journal of Environmental Science and Engineering B, a monthly professional academic journal, covers all sorts of researches on environmental management and assessment, environmental monitoring, atmospheric environment, aquatic environment and municipal solid waste, etc..

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Editorial Office:

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Ulrich's Periodicals Directory

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Summon Serials Solutions

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Subscription Information:

Price (per year):

Print \$600, Online \$480

Print and Online \$800

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Contents

Wastewater Treatment

- 391 **Low-Cost Technologies for Mining Wastewater Treatment**
Mike Agbesi Acheampong and Ebenezer David Okwaning Ansa

Environmental Biology

- 406 **Concentration and Biomagnification of Heavy Metals in Biota of the Coastal Marine Areas of Tanzania**
Sharifa Omar Bungala, John Ferdinand Machiwa and Daniel Abel Shilla

Environmental Mangement and Evaluation

- 425 **Evaluating Climate Change Effects on Natural Resources Using Remote Sensing Technologies: A Case of Kazimzumbwi Forest Reserve, Kisarawe in Tanzania**
Martine Hagai
- 431 **Modified Contingent Valuation Method for Agricultural Wastes between the Areas of Peloponnese and Thessaly in Greece**
Odysseas Kopsidas and Athanasios Kopsidas

Mining Activity Contribution

- 436 **Mining Contribution to Municipalities Development**
José Aroudo Mota, José Emanuel de Carvalho Nazário, Jorge Filipe dos Santos, José Oswaldo Siqueira and Paulo Cesar Horta Moreira

Low-Cost Technologies for Mining Wastewater Treatment

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Abstract: The mining industry has contributed tremendously to the global economy. However, waste generated by this activity poses many challenges. Current low-cost technologies for the removal of heavy metals from mining wastewater include biosorption, adsorption, CWs (Constructed Wetlands) and waste stabilization ponds. This chapter focuses on sustainable mining wastewater treatment technologies with emphasis on gold mining wastewater. It discusses the technical and environmental challenges associated with mining effluent treatment, process conditions for optimum plant performance, efficiency, limitations and the economics of treating mining wastewater. The overall treatment cost of metal contaminated wastewater depends on the process employed and the local conditions. In general, technical applicability, cost-effectiveness and plant simplicity are the key factors in selecting the most suitable treatment method. Proper management of the spent biosorbent and solid wastes generated is also discussed.

Key words: Removal, heavy metal, biosorption, waste stabilization pond, CW (Constructed Wetland), mining wastewater.

1. Introduction

Heavy metals occur in immobilized form in sediments and as ores in nature. Various human activities like ore mining and industrial processes disrupt the natural biogeochemical cycles causing increased deposition of heavy metals in terrestrial and aquatic environments. Heavy metals are found in wastewater discharged from industries such as mining, metal processing, electroplating, textile, tannery and petroleum refinery [1-5]. Heavy metals such as As, Cu, Pd, Zn, Fe, Cr, Ni and Hg are toxic [6-8] and therefore the discharge of untreated metal-laden effluent from the mining industry poses serious environmental challenges [9, 10]. Sorption using natural and agricultural materials has been proposed as a cost effective and environmentally friendly alternative to chemical treatment [11-14].

The discovery and further development of biosorption phenomena provide a basis for a whole

new technology aimed at the removal of various pollutants or the recovery of valuable resources from aqueous systems. Although there are many industrial processes using sorbents such as activated carbon, the development of biosorption processes is still mainly at the stage of laboratory studies in spite of enormous progress made over the last decade [15]. Most studies on continuous biosorption systems have focused mainly on the optimisation of operating conditions and breakthrough curves using synthetic metal solutions [16-21]. Many of these studies have limited industrial application because industrial effluents are more complex, containing several metal ions and other contaminants [22]. Singh, A., et al. [22] indicated that treatment of industrial effluent in continuous flow through systems allows the use of biosorbents for multiple biosorption and desorption applications. In this way, process sustainability is achieved through a substantial reduction in the fresh sorbent requirement, operational cost and solid waste materials needing disposal or containment [4, 15].

WSPs (Waste Stabilization Ponds) are common technologies for industrial wastewater treatment due

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to their low capital and operating costs. They are particularly popular in locations where large tracts of land are available and affordable. In spite of the popularity of WSPs, limited studies on the use of this technology for the removal of heavy metals from mining wastewater had been conducted [23]. The few studies conducted on WSPs have shown a poor performance in the removal of metals [23-25]. Due to this limitation of scanty literature availability, greater attention is paid to the use of CWs (Constructed Wetlands) for mining wastewater treatment.

CWs are artificial or engineered wetlands developed to utilize the natural, physical, biological and chemical processes that take place in these aquatic ecosystems involving the soil, flora and fauna, including its microbial communities, to treat wastewater [26]. The use of CWs for the removal of heavy metals is a very recent development. CWs are used for the treatment of wastewater from mining, oil refineries, chemical factories, pulp and paper production, tannery, textile, abattoir, distillery, winery and other industries as well as various runoff waters from airports and highways as various sources of industrial wastewater, noting limited studies done on wastewater from mines [26]. This is because the treatment of wastewater from mines had not been given much attention in literature [27], as results that monitoring programmes by mining companies are usually not published in peer reviewed journals.

2. Technological Options for the Removal of Heavy Metal from Mining Wastewater

Currently, sustainable technologies for the removal of heavy metals from mining wastewater include biosorption, adsorption, CWs and waste stabilization ponds, among others.

2.1 Biosorption

Wang, J. and Chen, C. [28] defined biosorption as the removal of metal and metalloid species,

compounds and particulates from solution by biological material. Biosorption is made possible by the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical uptake pathways.

2.1.1 Understanding Metals Biosorption Mechanism during Mining Wastewater Treatment

Due to the interaction of several factors on specific biosorbents, it is almost impossible to propose a general mechanism. Although several metal-binding mechanisms have been put forward, e.g. physical and chemical adsorption, ion exchange and microprecipitation, the actual mechanism of metal biosorption is still not fully understood [29].

Ion-exchange is an important concept in biosorption, because it explains many observations made during heavy metal uptake experiments [30]. Ion-exchange is a reversible chemical reaction where an ion within a solution is replaced by a similarly charged ion attached onto an immobile solid particle [31]. This ion-exchange process is one of the well-known surface reactions, which represents a great degree of complexity, primarily due to its multi-species nature. In bacterial biosorption, the bacterial cell wall is the first component that comes into contact with the metal, where the solute can be deposited on the surface or within the cell wall structure [32]. Since the mode of solute uptake by dead or inactive cells is extracellular, the chemical functional groups of the cell wall play vital a role in biosorption.

Another frequently encountered metal binding mechanism is chelation, which can be defined as a firm binding of metal ions with an organic molecule (ligand) to form a ring structure [29]. Various functional groups including carboxylic, hydroxyl, sulphate, phosphate, amides and amino groups can be considered possible for sorption. Among these groups, the amino group is the most effective for removing heavy metals, since it does not merely chelate cationic metal ions but also absorbs anionic species through the electrostatic interaction or hydrogen bonding. As

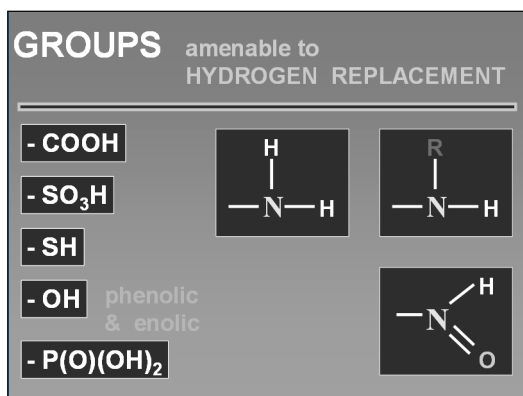


Fig. 1 Major binding groups for biosorption [33].

they are negatively charged and abundantly available, carboxyl groups actively participate in the binding of metal cations [34]. Fig. 1 shows major functional groups involve in metal binding.

Agricultural and plant waste materials, such as coconut husk and shell, are usually composed of lignin and cellulose as the main constituents. Other components present in the metal binding process are hemicellulose, lipids, proteins, simple sugars, starches, water, hydrocarbons and many more compounds that contain a variety of functional groups [35]. The presence of these functional groups and their complexation with heavy metals during biosorption has been reported by different researchers using spectroscopic techniques.

Benavente, M., et al. [10] reported the treatment of gold mining wastewater using chitosan and found that the removal of Cu, Pb and Zn was not affected by the presence of other metals because they were present at low concentrations. The speciation of metallic ions in gold mining tailings wastewater depends on their oxidation states, the metallic ion concentrations, the cyanide concentration, the redox potential, the temperature and pH of the wastewater [10]. Benavente, M., et al. [10] indicated that the presence of cyanide had a negative impact on the sorption process, but not to the extent of affecting the removal of copper significantly, as evident from the low copper concentration ($< 0.01 \text{ mg}\cdot\text{L}^{-1}$) in their treated effluent. Similar to the findings of Benavente, M., et al. [10],

Acheampong, M. A. and Lens, P. N. [36] observed that neither the presence of cyanide nor other heavy metals inhibited the removal of copper from gold mining effluent studied.

According to Saad, D. M., et al. [37], metal-cyanide complexes and free metallic ions were mainly present in the gold mining wastewater at pH 7.7. They indicated that the speciation results for the tailings dam show that copper, lead and zinc were mostly found as free metallic ions with only a small fraction present as metal-cyanide complexes. This is, however, contradictory to well-established experimental science of metalocyanide species in tailings waters. The most commonly encountered iron cyanide complexes are the two formed with ferrous and ferric iron, $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$, respectively [38]. The Fe(III) complex being the predominant species is found in mining tailings solutions. The formation of hexacyanoferrate(III) is primarily the result of the oxidation of hexacyanoferrate(II) in surface impoundments. However, typically within solid tailings environment, the oxidation potential would result in the formation of ferrocyanide precipitates [39]. The hexacyanoferrates are classified as “inert” complexes, in that their chemical stability results from extremely slow rates of dissociation and relatively low toxicity [38]. The overall effect is the reduction in the free metallic ions present and an increase in the proportion of the metal-cyanide complexes in the tailings solutions.

When present in cyanide tailings solutions, copper is predominantly present as a mix of three forms: $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$ and $\text{Cu}(\text{CN})_4^{3-}$ [39]. The Cu(II) cyanide species are unstable in aqueous solution and disproportionate to the Cu(I) cyanides. While the formation of metal cyanide complexes does not completely eliminate the toxicity of cyanide, it does effect a substantial reduction in such toxicity. Metal cyanide complexes are also intermediates involved in the formation of more stable compounds that remove free cyanide from the tailings environment. Kunz, R. G., et al. [40] described a process where copper was

complexed with cyanide to enhance the adsorption and oxidation of cyanide onto activated carbon. The environmental significance of complexation of cyanide with heavy metals is that it is relatively rapid and it occurs wherever soluble species of these metals are present, such as found in gold mining tailings. It reduces the toxicity of free cyanide and acts as an intermediary to reduce cyanide mobility via adsorption onto organic and inorganic surfaces or precipitation of metal cyanide salts [39].

In treating electroplating wastewater using sugar cane bagasse, Sousa, F. W., et al. [12] reported a considerable decrease in adsorption of zinc and nickel, probably due to electrostatic repulsive forces between the cationic sugar cane bagasse surface and the metal ions. In contrast, Acheampong, M. A. and Lens, P. N. [36] reported that coconut shell used in their study was negatively charged at the gold mining effluent pH due to the lower point of zero charge pH of 6.5. Ahmed, M. J. K. and Ahmaruzzaman, M. [41] suggested that the removal of the positively charged heavy metals from gold mining effluent could be enhanced by electrostatic attraction forces between the biosorbent and the sorbate.

2.1.2 Process Conditions

The investigation of factors affecting the efficiency of heavy metal sorption is of great interest for the industrial community. The efficiency is strongly influenced by the physico-chemical characteristics of the solutions, such as pH, temperature, initial metal concentration, presence of other ions and sorbent dosage [42]. These factors are important in evaluating the maximal sorption performance of any sorbent. The solution pH is a crucial factor in heavy metal sorption. The pH value significantly influences the dissociation of the sorbent and the solution chemistry of the heavy metals, i.e. metal speciation, hydrolysis, complexation by organic and/or inorganic ligands, redox reactions and precipitation are all pH dependent [29, 43, 44]. Competition between cations and protons for binding sites means that sorption of metals like Cu, Cd, Ni, Co

and Zn is often reduced at low pH values [42]. Due to the importance of pH in sorption, many researches were conducted on its effect on the removal of various heavy metals.

Depending on the structure and surface functional groups of a sorbent, temperature has an impact on the adsorption capacity within the range of 20-35 °C [45]. It is well known that a temperature change alters the adsorption equilibrium in a specific way determined by the exothermic or endothermic nature of a process [29]. Higher temperatures usually enhance sorption due to the increased surface activities and kinetic energy of the solute. However, physical damage can be expected at higher temperatures [32]. It is always desirable to evaluate the sorption performance at room temperature, as this condition is easy to replicate.

Another important parameter in biosorption is the ionic strength, which influences the adsorption of solute to the biomass surface. Industrial wastewater often contains ions other than heavy metal ions, e.g., Na^+ , K^+ , Mg^{2+} and Ca^{2+} , which may interfere with heavy metal ion uptake by biomass. As a general trend, the metal uptake is found to decrease with increasing ionic strength of the aqueous solution as a result of more electrostatic attraction and change of the metal activity [29, 43, 46, 47].

The amount of biomass in the solution also affects the specific metal uptake. For lower values of biomass concentrations, there is an increase in the specific uptake [48]. Gadd, G. M., et al. [48] suggested that an increase in biomass concentration leads to interference between the binding sites. By increasing the adsorbent dosage, the adsorption efficiency increases even though the amount adsorbed per unit mass decreases. In principle, with more adsorbent present, the available adsorption sites or functional groups also increase. In turn, the amount of adsorbed heavy metal ions increases, which results in an improved adsorption efficiency [29, 49-52].

The size of the biosorbent also plays a vital role in biosorption. Smaller sized particles have a higher

surface area, which in turns favours biosorption and results in a shorter equilibrium time. Simultaneously, a particle for biosorption should be sufficiently resilient to withstand the application of pressure and extreme conditions applied during regeneration cycles [53]. Therefore, preliminary experiments are necessary to determine the suitable size of a biosorbent.

2.1.3 Process Configuration

Due to the concentration difference driving force for sorption (between the sorbate in the solution and that already sequestered), generally the most effective configuration of the sorption system is that based on a flow-through fixed bed type of a reactor/contactor (Fig. 2). The sorption column would generally not exceed approximately 1.8 m in diameter and 4-5 m in height. The scaling up of the process to accommodate larger flows is attained by simply multiplying the number of columns that would operate in parallel. Rarely, usually because of special process requirements, a mixed contactor could also be used. Different, usually multi-stage, counter-current configurations could then be arranged. The most

important criterion in the design of fixed-bed sorption systems is the prediction of the column breakthrough or the shape of the adsorption wave front, which determines the operating life-span of the bed. Fig. 2 shows a typical of fixed-bed sorption systems for treating gold mining effluent.

2.1.4 Process Performance

The overall performance of the processes based on the sorption column mode of operation is judged by the column operating time (until the column sorption capacity is exhausted), characterized by the sorbate break-through point as determined at the column exit (Fig. 3). Since the fixed-bed column does get eventually saturated, a process arrangement is often used whereby one column is in active sorption operation while another one is being prepared (regenerated and cleaned) during its stand-by period. That column preparation usually consists of elution of the sequestered sorbate with simultaneous or sequential sorbent regeneration, clean-up and washing. Sorbent regeneration capacity is an important characteristic that results in a better overall process economy.

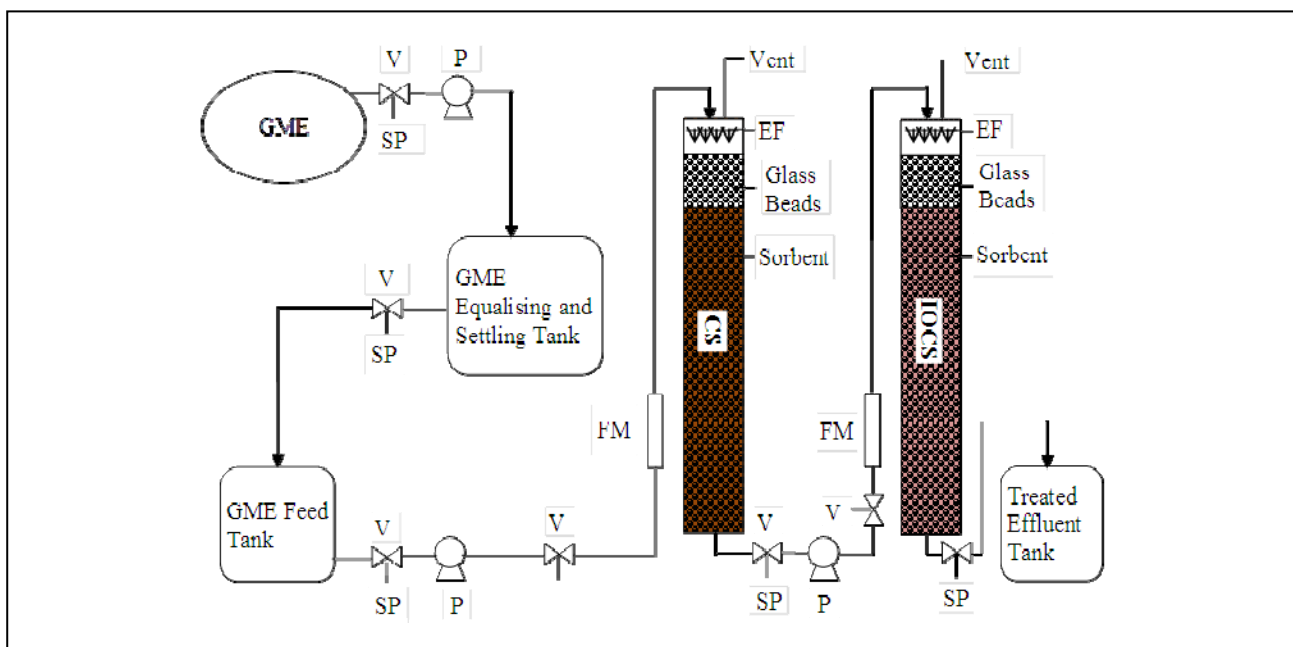


Fig. 2 Schematics diagram of a two-stage pilot plant set-up for treating gold mining effluent (CS: Coconut Shell; IOCS: Iron Oxide Coated Sand; EF: Effluent Distributor; P: Pump; SP: Sampling Point; V: Valve; GME: Gold Mining Effluent; FM: Flow Meter) [36].

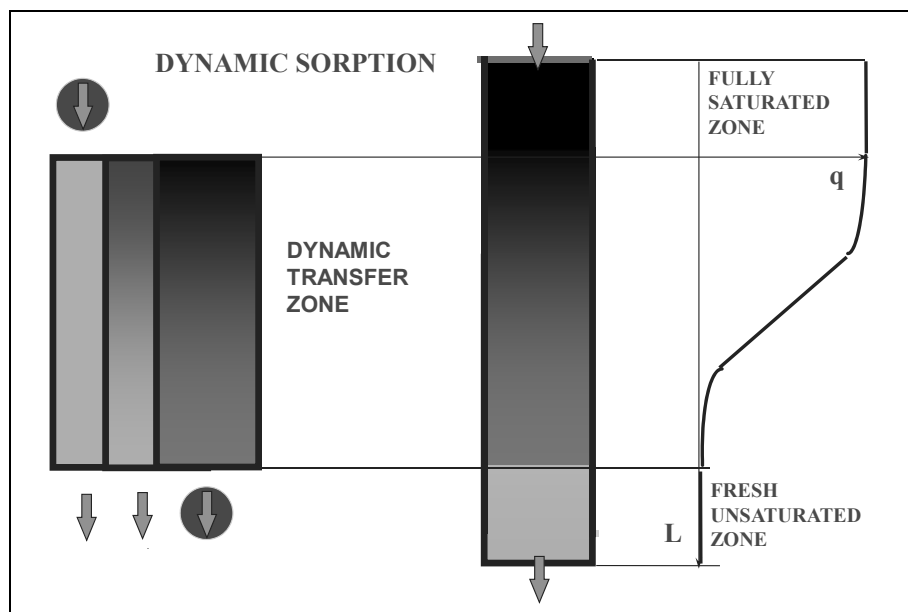


Fig. 3 Schematic representation of the development of dynamic transfer zone in the continuous-flow fixed bed sorption column [36].

2.1.5 Sorbent Regeneration and Metal Recovery

One of the main attributes of biosorption is the potential of sorbent regeneration and metal recovery [52, 54]. Desorption of sorbed metals from loaded sorbent enables reuse of the sorbent and recovery and/or containment of the sorbed metals from a highly concentrated eluant stream [42, 52]. In some cases, desorption treatment may further improve the sorption capacities [55], although in other cases there may be a loss of sorption efficiency and even a complete disintegration of the biosorbent [56]. To improve process viability, better understanding of the sorption-desorption processes in sorbent regeneration is needed. The acid-based metal desorption may be followed by further steps to prepare the biosorbent for the most efficient subsequent uptake cycle. This may entail pre-saturating the active sites of the biomaterial with more pH-neutral calcium or potassium cations in order to avoid an uncontrollable acidic wave inside the column caused by the release of ion-exchanged protons. Some overall process optimization may be useful in this respect.

Metal recovery is a down-stream consideration that has been added to the metal removal aspect, which is driven predominantly by environmental detoxification

considerations. The sorption and desorption processes offered the opportunity for an economical recovery of metals from the concentrated solution. The feasibility of the recovery operation depends, to a large degree, on the type of recovery procedures used. The spent sorbents generated at the end of the process must be properly and safely disposed. Various disposal options that are in conformity with local solid waste management practice are employed.

2.1.6 Process Integration

For a successful industrial application biosorption technology for the sustainable treatment of mining wastewater, the integration of the sorbent processing and formulation, sorption-desorption application, metal recovery for reuse and the disposal of the spent biomass (Fig. 4) is very critical. Where the treated effluent does not meet the regulatory discharge requirement, a further polishing step using WSPs and CWs is applied.

2.2 WSPs and CWs

The extraction of metals such as gold, zinc, lead, copper, iron, aluminium and many others involves the release of many contaminants that may pose serious threat to public health or wildlife and therefore had to

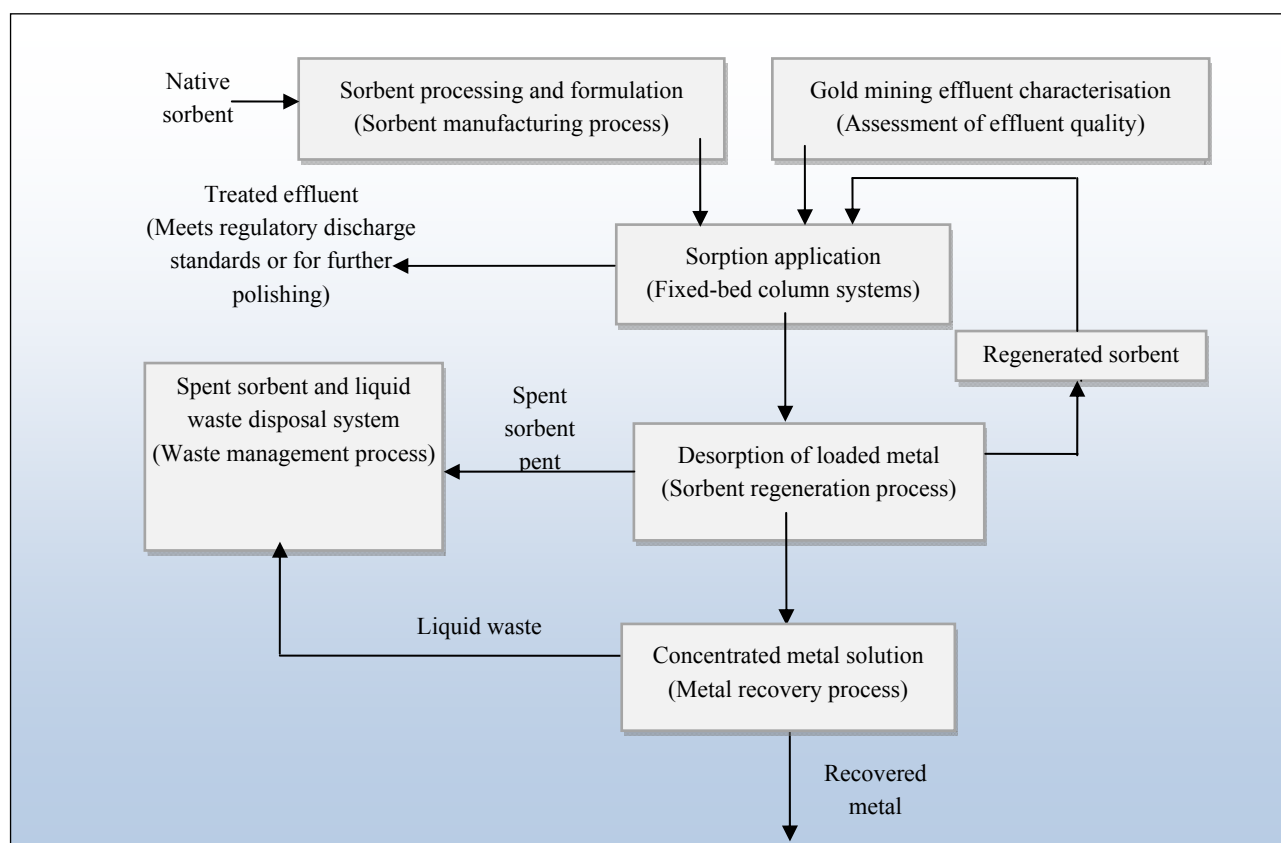


Fig. 4 Generalised integrated single stage sorption systems for gold mining effluent treatment using locally available low-cost materials.

be removed or converted to various forms that are not toxic. The contaminants include heavy metals such as zinc, copper, lead, chromium, iron and manganese, cyanide, phosphate, carbonates, sulphides, sulphates, arsenic and its complexes, nitrogen and its compounds [57]. A detail list of the concentrations of the constituents of typical mining activity wastewater is outlined in Table 1.

WSPs are common technologies for wastewater treatment due to their low capital and operating costs. They are particularly popular in locations where large tracts of land are available and affordable. In spite of the popularity of WSPs, very limited studies on the use of this technology for the removal of heavy metals as pertains in mining wastewater had been conducted [23]. The few studies conducted on WSPs have shown a poor performance in the removal of metals [23-25]. Due to this limitation of scanty literature availability, greater attention would be paid to the use of CWs.

CWs are artificial or engineered wetlands developed to utilize the natural, physical, biological and chemical processes that take place in these aquatic ecosystems involving the soil, flora and fauna, including its microbial communities to treat wastewater. The use of CWs for the removal of heavy metals is a very recent development. In his review of the use of CWs in industrial wastewater treatment, Vymazal, J. [26] mentioned the oil refineries, chemical factories, pulp and paper production, tannery and textile industries, abattoir, distillery, winery and other food processing industries as well as various runoff waters from airports and highways as various sources of industrial wastewater, noting limited studies done on wastewater from mines. This is because the treatment of wastewater from mines had not been given much attention in literature [27], as results that monitoring programmes by mining companies are usually not published in peer reviewed

Table 1 Typical constituents of wastewater from different mining activity [57, 62, 63].

Key parameters	Sources of wastewater		
	Gold mining	Zinc and lead mining	Zinc-rich acid mine drainage
pH	701-8.6	8.23	3.58
Conductivity	94-979 mS/m		1,915 μ S/cm
TSS		2,495 $\pm$ 182 mg/L	
Mg	31-1,488 mg/L		19.0 mg/L
Ca			136 mg/L
Li	0.22-2.8 mg/L		
Na	14-114 mg/L		14.3 mg/L
K	4.7-114 mg/L		12.3 mg/L
Al			12.2 mg/L
As	41-40 μ g/L	0.077 $\pm$ 0.024 mg/L	
Sb	35-160 mg/L		
Zn		14.47 $\pm$ 8.37 mg/L	552 mg/L
Pb		11.49 $\pm$ 7.7 mg/L	
Hg		0.0003 $\pm$ 0.0002 mg/L	
Ni	37-69 μ g/L		
Cd		0.05 $\pm$ 0.04 mg/L	
Fe	67-109 μ g/L		
Mn	0.42-1.3 mg/L		17 mg/L

journals. Most literatures on this subject, therefore, are experiments conducted at the microcosm and pilot scales. This notwithstanding, a few studies had been documented. For example, Pantano, J., et al. [58] were successful in using a horizontal flow CW to remove Cd, Zn and Cu from mining impacted groundwater while Gerth, A., et al. [59] used a hybrid free water surface and horizontal flow CW to treat seepage water from a uranium mine in Germany.

2.2.1 Treatment Performance and Limitations

The removal of toxic metals from mining wastewater using physico-chemical approaches such as adsorption, oxidation and reduction and chemical precipitation require large quantities of chemical reagents and produce a considerable amount of toxic sludge and secondary pollutants, thus raising questions about the sustainability of these technologies [27]. Conventional wastewater treatment systems such as the activated sludge treatment system are known to perform better in the removal of heavy metals than WSPs.

One limitation of WSPs in heavy metal removal is its inability to overcome shock loadings due to the low

presence of microorganisms [24]. This limitation was overcome by the introduction of attached growth medium which resulted in significant increase in heavy metal removal [25]. In the absence of such modifications, WSPs had to operate at very low organic loadings for metal removal. The use of CW in treating mining wastewater is also limited to the polishing stages of treatment as influent of high suspended solids can lead to clogging.

Ustun, G. E. [23] reported in a study involving nine metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) that while the WSP removed over 50% in Al and Cr, for the other metals removals were less than 20% compared with the activated sludge system which a range of removals from 47% in Ni to 95% for Cr. Polprasert, C. and Charnpratheep, K. [25] observed that when a medium is provided in WSPs for the adsorption of metals, the performance of the WSPs can increase significantly. Sekomo, C. B., et al. [60] using synthetic wastewater, however, reported a removal rate of Cr of 94% and 98% for a duckweed and algal pond systems respectively. The researchers noted that the rates of removal obtained occurred

irrespective of the loading rate or the light regime. In that same study, using a light-darkness regime of 16 h light/8 h darkness, Sekomo, C. B., et al. [60] recorded a Zn removal rate of 70% at a lower loading rate, which dropped to a removal rate of 40% when the loading rate was increased. The removal efficiency rose back to 80% at the higher metal loading rate but under 24 h light regime. Pb, Cd and Cu all showed relatively similar patterns with removal efficiencies of 36% and 33% for Pb, 33% and 21% for Cd and 27% and 29% for Cu in the duckweed and the algal ponds, respectively in that study. In biological wastewater treatment, metal removal efficiency depends on the metal species and concentration, the reactivity of the available biopolymers or biomass and the composition of other wastewater components [61]. Sekomo, C. B., et al. [60], however, observed that in spite of the physico-chemical differences among the duckweed and algal ponds, differences in metal removal efficiency between algal and duckweed ponds were rather small. As Table 2 shows, CW offers a viable alternative for the removal of metals from mining wastewater.

2.2.2 Mechanisms of Metal Removal

In waste stabilization ponds, the removals of metals occur through a process of adsorption unto suspended solids and biomass, with subsequent sedimentation of adsorbed metals. This takes place mainly in the anaerobic pond and to some extent the facultative ponds. The metal removal efficiency depends on the metal species and concentration, the reactivity of the available biopolymers or biomass and the composition of other wastewater components [61]. Thus the formation of metal complexes and dissolution values for each metal are different resulting in varying removal efficiency for each metal type [66]. As mentioned earlier, the low amount of medium for adsorption by metals in WSPs limits the extent of its removal in WSPs.

Mechanisms involved in heavy metal removal in CWs, include a combination of sedimentation, filtration, binding to substrata, precipitation as

insoluble salts such as sulphides or oxyhydroxides and accumulation by plants, algae and/or bacteria [67].

It has been argued that substrates act as primary sink for heavy metal accumulation and that the bulk of the influent heavy metal is removed by accumulation in the ground biomass and not the above ground biomass of plants [27, 68].

Heavy metal uptake varies from one plant species to another in CWs. However, Yadav, A. K., et al. [27] noted that in all three plant species involving *Canna indica*, *Typha angustifolia* and *Cyperus alternifolius* in a VSSF (Vertical Subsurface Flow), the contribution of the below ground biomass (roots) was more than the above ground biomass (leaves and stem) in the removal of Cu, Cr, Co, Ni and Zn from aqueous solution. They also noted that the removal of Cr, Ni, Cu, Zn and Co was enhanced by 16.6%, 22.9%, 20.4%, 21.5% and 21.8% respectively, when gravel bed depth of CWs was increased from 0.3 m to 1.5 m, showing that enhanced gravel bed depth may improve the performance of CWs in metal removal.

In addition to taking up metal, the root network also filters fine particulate matter, for which sedimentation is slower than for larger particles. Through the biofilm that forms on the surface of the roots, significant biological activity develops and could intervene in the process of biodegradation of other pollutants, such as hydrocarbons [69].

It has been suggested that plants used for the uptake of heavy metals must be mowed yearly to harvest biomass and recover pollutants and these plants used for providing fuel [69].

2.2.3 Economics of Heavy Metal Removal

In determining the suitability of a technology for treating wastewater, key considerations are given to its robustness while meeting effluent standards, extent of chemical usage and the degree of environmental nuisance it poses, capacity for various re-use options as well as environmental benefits, greenhouse gas emissions and its energy and capital requirements [70, 71]. The high purification rates [72, 73], robustness

Table 2 Performance of various types of CWs in the removal of metals from mining wastewater.

Metal/CW type	Influent concentration (mg/L)	Retention time	Removal (%)	Literature reference
Al/VSSF	0.51	79 days	100.0	[64]
As/HSSF	2.3	11 days	99.9	[65]
Zn/VSSF	3.19	36 days	100.0	[64]
Zn/VSSF	20.0	72 hours	99.3	[27]
Zn/HSSF	14.5	5-7 days	97.3	[63]
Pb/VSSF	0.0105	36 days	100.0	[64]
Pb/HSSF	11.5	5-7 days	99.0	[63]
Ni/VSSF	20.0	72 hours	76.4	[27]
Cd/VSSF	0.0066	36 days	100.0	[64]
Cd/HSSF	0.05	5-7 days	94.0	[63]
Fe/HSSF	97.3	11 days	96.1	[65]
Mn/VSSF	0.206	79 days	100.0	[64]
Co/VSSF	20.0	72 hours	54.6	[27]
Cu/VSSF	20.0	72 hours	68.3	[27]
Cu/VSSF	0.73	30 days	100.0	[64]
Cr/VSSF	20.0	72 hours	66.2	[27]

Note: HSSF CW: Horizontal Subsurface Flow Constructed Wetland; VSSF CW: Vertical Subsurface Flow Constructed Wetland.

and operational stability [74, 75], low skilled manpower and capital requirement [76, 77], ecological benefits [71, 75-79] as well as direct economic benefits such as fish farming [75, 76] of WSPs and CWs are well documented in literature. For the treatment of mining wastewater, however, particular importance is attached to the energy requirement as well as the carbon footprint of the treatment technology.

3. Energy Requirement

Adequate water supply is important for mining operations and as water is one of key business risks for the industry [80], the use of sustainable technologies that treat and use water efficiently is a must. Using the LCA (Life Cycle Analysis) approach, Brix, H. [81] compared the energy requirements of three system types namely, CWs, wastewater aquaculture facilities and conventional wastewater treatment technologies. The results revealed that the CWs require very low energy compared to the others. Austin, D. and Nivala, J. [82] investigated the energy requirements of three wetland technologies: aerated subsurface flow, tidal flow and pulse-fed wetland

treatment as engineered wetlands, and compared them to that of a mechanical activated-sludge treatment system. Their results showed that the electrical power requirements for the wetland systems were 0-56% of that of activated-sludge treatment systems. These findings agreed with a study by Zhou, J. B., et al. [83], which used a different approach involving emergy synthesis. Emergy is described as the available energy of one kind previously required to be used up directly and indirectly to make a product or service [84, 85]. Shao, L., et al. [86] in adopting the input-output energy approach of system accounting estimated that the energy embodied in treating per m³ of wastewater and removing per kg BOD (Biochemical Oxygen Demand), COD (Chemical Oxygen Demand), SSs (Suspended Solids) and NH₃-N by a CW is only 6.83%, 17.48%, 13.96%, 22.47% and 9.48% respectively of that by a conventional system. Studies that compare the energy requirement of WSPs and CWs for treating mining wastewater is rare but Mara, D. D. [87] showed that on the basis of land area requirement, capital, operating and maintenance costs, WSPs are to be preferred to SSF (Surface Flow) CW. As CWs perform better in metal removal than WSPs,

it can be argued that to obtain a performance equal or better than that of a CW, more energy, land area may be required. Thus a key research question would be how much more energy would be required.

4. Greenhouse Gas Emissions

One of the factors to consider in assessing the economic viability of a wastewater treatment technology is its carbon footprint. Mander, U., et al. [88] noted that the emission factor of methane in FWS (Free Water Surface) and HSSF CWs is very high and yet the absolute value of methane emission is relatively small in the order of 1-2 magnitudes lower than that found in conventional wastewater treatment plants. In their review, they further observed that carbon dioxide emission in FWS CW was significantly lower than that of SF (Subsurface Flow) CWs while methane emission in VSSF CWs was also lower than in HSSF CWs. However, in that same study, no real differences were observed among the various types of CW in the emission of nitrous oxide. The median values for FWS, VSSF and HSSF CWs were $0.09 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, $0.12 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and $0.13 \text{ mg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, respectively.

Sims, A., et al [89] showed that a duckweed covered WSP emitted 504-1,900 mg methane and 1,700-3,300 mg carbon dioxide $\text{m}^{-2}\cdot\text{d}^{-1}$. FWS CW resembles WSPs in its biochemical and physical processes [90] and is therefore likely that emissions in FWS and WSPs may be similar. Studies comparing the emission rates of GHG (Green House Gas) in these treatment technologies using the same source of wastewater are rare.

GHG emissions in WSPs and CWs can be affected by various operating conditions. Methane flux properties, activities of methanogens and methanotrophs and the relationship between methane flux rate and some environmental parameters are known to be different in different plant species of CW systems. The difference in emission intensity varied with the different vegetation cover and seasonal

fluctuations [91]. In that same study by Wang, Y., et al. [91], they noted that, for the same aquatic plant species, the difference in emission intensity varied with influent pollutant concentrations, the methane emission data showing large spatial and temporal variation ranging from 0 to $16.76 \text{ g CH}_4 \text{ m}^{-2}\cdot\text{day}^{-1}$ with higher emissions occurring when influent loadings are high. Mander, U., et al. [88] also noted that overloading a HSSF CW led to elevated methane emissions. Further studies on GHG emissions for treating mining wastewater is necessary, taking into consideration variations created by hydrological regimes, microbial communities and plant species.

5. Concluding Remarks

Pollution of the environment with heavy metals is widespread and often involves large volumes of wastewater. Remediation strategies for mining wastewater must be designed to support high throughput while keeping costs to a minimum. Biosorption is an alternative to traditional physicochemical means for removing toxic metals from wastewater. Biosorption can quickly and effectively remove dissolved metals out of dilute complex solution with high efficiency. These characteristics make biosorption an ideal candidate for the treatment of high volumes of low concentration complex mining wastewater. However, preparing biosorption for application as a process requires a strong chemical engineering background, and an understanding of the sorption operation is a must. Research showed that the down-flow fixed-bed treatment configuration is an ideal system for the simultaneous removal of heavy metals from low concentration mining effluent. For industrial application of biosorption, regeneration of the biosorbents is important in keeping the process costs down and opening the possibility of recovering the metal ion extracted from the liquid phase. Where the treated effluent characteristic did not meet the discharge requirement, CW and WSP treatment

system can be used to polish the effluent from the biosorption system.

Studies conducted on the use of CWs and WSPs in particular for treating mining wastewater are few. Available evidence suggests that WSPs perform poorly in metal removal due to the low density of suspended solids in the treatment system as removal is mainly through adsorption onto suspended solids. The introduction of attached growth medium into the pond system therefore can result in significant increase in heavy metal removal. This growth medium can also increase WSPs ability to overcome shock loadings. CWs, however, perform better in heavy metal removal than WSPs. The removal efficiency of CWs however is known to be affected by the metal species and concentration, the reactivity of the available biopolymers or biomass, and the composition of other wastewater components as well as its exposure to sunlight. The formation of metal complexes and dissolution values for each metal species are different resulting in varying removal efficiency for each metal type. In terms of cost of treatment, a key consideration is the energy requirement and its greenhouse gas emissions.

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Concentration and Biomagnification of Heavy Metals in Biota of the Coastal Marine Areas of Tanzania

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Abstract: The concentrations of heavy metals (As, Hg, Cr, Pb and Zn) were measured in the macroalgae, macrobenthos and fish from the Tanzanian coastal marine environment in order to ascertain the biomagnification using stable isotopes of C and N. Macroalgae samples from the central marine areas of the Tanzanian coast had higher mean concentrations of Hg ($0.17 \pm 0.01 \mu\text{g/g}$) and Cr ($23.7 \pm 4.15 \mu\text{g/g}$) compared to other locations. Higher concentration of Hg ($0.06 \pm 0.02 \mu\text{g/g}$) was detected in the *Ulva fasciata* close to the Msimbazi Creek in Dar es Salaam, whereas the highest concentration of Cr ($45.5 \pm 6.83 \mu\text{g/g}$) was found in *Ulva petrusa* near Dar es Salaam port. The crab *Portunus pelagicus* collected from Pangani river estuary contained $411.5 \pm 13.04 \mu\text{g/g}$ of Zn. The other metals were uniformly distributed in macrobenthos from the entire coast. Mercury and lead in the biota were found to biomagnify along the *Arius dussumieri* and *Lethrinus lentjan* food chains as suggested by the significant positive relationships between log-pollutant concentrations in fish muscle tissues vs. $\delta^{15}\text{N}$ signatures. Zinc in muscle tissues was found to be transferred along the food webs although no biomagnification was observed. Arsenic and chromium were found to decrease with the rise of the trophic position. Metal concentrations in macroalgae, macrobenthos and fish were compared with quality guidelines values by FAO (Food and Agricultural Organization) in 1983 and they all were below permissible limits for human consumption.

Key words: Heavy metals, food chains, bioconcentration, biomagnification, stable isotope ratios, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, TL (Trophic Level).

1. Introduction

The term bioaccumulation refers to the net accumulation of a chemical by an aquatic organism as a result of uptake from all environmental sources (water, food and sediment). Bioaccumulation can be viewed as a result of competing rates of chemical uptake and elimination (chemical loss) by aquatic organisms. When the rates of chemical uptake and elimination achieve balance, the distribution of the chemical between the organism and its source(s) is said to be at steady-state [1]. Under steady-state conditions, a BAF (Bioaccumulation Factor) is defined as the ratio of the concentration of a chemical in the tissue of an aquatic organism to its concentration in water, in situations where both the organism and its food are exposed [1]. Aquatic organisms accumulate and retain certain chemicals

when exposed to these chemicals through water, their diet and sediments [2].

Biomagnification therefore is a process where chemical substances are transferred from food to an organism resulting in higher concentrations compared with the source [3-5]. Biomagnification can also be defined as the increase in concentration of chemicals between TLs (Trophic Levels). If the biomagnification factor (concentration in predator/concentration in prey) is greater than one, then the element is biomagnified in the body of a predator.

At the first TL, only direct accumulation of heavy metals from the water occurs. In considering phytoplankton, the degree of pollutant association with the cell is generally directly related to the extracellular concentration. Dead cells concentrate metals comparable to living ones indicating that the initial association of a metal with the cells is governed by adsorption [6]. Bioconcentration is the uptake of contaminant from water by aquatic organisms where water is the only pathway and is measured as a BCF

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(Bioconcentration Factor). The BCF is most useful for low TL organisms such as phytoplankton and macroalgae, which are in rapid equilibrium with chemicals with low $\log K_{ow}$ (up to 5) in water [7]. BCFs do not account for biomagnification of chemicals in the food webs [8]. Hence for larger, higher TL organisms, BCF has been shown to underestimate bioaccumulation potential for hydrophobic compounds that have $\log K_{ow}$ values greater than or equal to 4.5 [8].

The role of food chains in carrying contaminants to top predator fish which is a possible source for human dietary exposure, has received attention for several decades [9-15]. The trophic transfer (trophodynamics) of elements along a food chain can result in an increase (biomagnification), a decrease (biodilution) or even may cause no change in elemental concentration along that particular food chain [16]. The trophodynamics of mercury (Hg) has been well studied and shows consistent biomagnification trends [12-15]. Other elements such as iron have been reported as not biomagnifying in food webs [9]. For other elements such as rubidium, selenium, cadmium, copper, zinc and silver, there is a growing number of studies demonstrating their biomagnification depending on site and metal-species specific factors [17-19]. Due to the deleterious effects of metals to aquatic ecosystems, it is necessary to monitor their levels in key species, because this will give an indication of the temporal and spatial extent of the accumulation and biomagnification as well as an assessment of the potential impact to human health [17].

Stable isotopes analysis has been used to study the ecological significance of materials from different sources in permanent lakes [5, 20], streams and rivers [10, 11], estuaries and bays [21, 22] and seas [23, 24]. This technique has also been used to describe trophic relationships between animals in a variety of terrestrial [25], fresh water [26] and marine [27, 28] environments. However, the great majority of these

studies have been conducted in temperate systems, and information on the sources of energy and food web structure in tropical aquatic systems in general and in estuaries of Tanzania in particular is still lacking. TP (Trophic Position) can be related with contaminant concentrations in order to trace the pathways of contaminant biomagnification by top predators in aquatic and terrestrial food webs [14, 29, 30]. Net bioaccumulation of an element occurs when its trophic transfer is greater than that of carbon and the concentration thus increases with increasing TL [31, 32].

In this study, accumulation of heavy metal As, Hg, Cr, Pb and Zn in macroalgae, macrobenthos and fish were analysed to determine biomagnification in the food chains of the marine catfish *A. dussumieri* and the snapper *L. lentjan*. The study sought to ascertain the safety of sea food from the coastal marine areas of Tanzania.

2. Materials and Methods

2.1 Study Area

This study was executed in the coastal waters of Tanzania in the western Indian Ocean. The coastal area of Tanzania (Fig. 1) encompasses a number of habitats that include coral reefs, mangroves, seagrass beds, sand banks, wetlands and beaches which support various resources both living and nonliving, and provides life support to coastal communities where such activities as fisheries and related activities play an important role in the social and economic development of local communities. The coastal areas (Dar es Salaam, Tanga, Zanzibar and Mtwara) are faced with expanding populations and emerging land-based activities such as agriculture, mineral exploitation and industrial activities which exert pressures on coastal waters, thus negatively affecting water quality. It receives water from both rivers as well as large amounts of domestic and industrial effluents. The studied area are also characterised by local harbour activities while at Dar es Salaam port

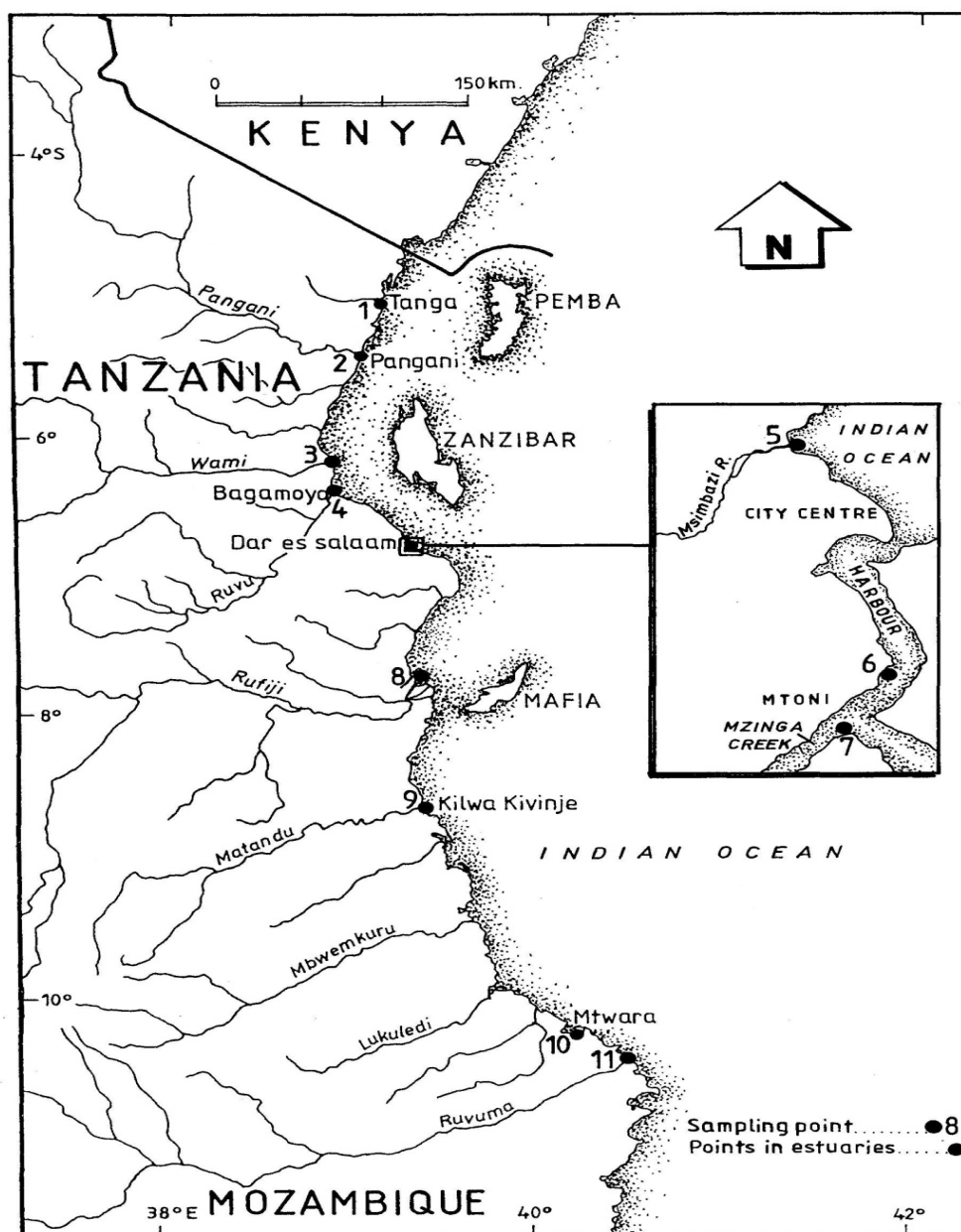


Fig. 1 Map of the marine coast of Tanzania showing the eleven sampling stations.

area, Mtwara port area and Tanga port area, there are harbour and ship fumigation activities and also loading and offloading of different types of cargo.

2.2 Establishment of the Sampling Stations

Eight sampling stations were located in the estuarine of rivers and three in marine areas near ports. Water, sediments and biota were collected from estuaries of these rivers: Pangani, Wami, Ruwu, Mzingi, Msimbazi, Rufiji, Matandu and Ruvuma (Fig.

1). The port areas from which samples were collected were Dar es Salaam, Tanga and Mtwara (Fig. 1). The positions of sampling stations were determined using a Geographical Positioning System (Garmin GPS 72), as shown in Table 1. Three sites were established which are NCMA (Northern Coastal Marine Areas) (stations 1, 2, 3 and 4), CCMA (Central Coastal Marine Areas) (stations 5, 6 and 7) and SCMA (Southern Coastal Marine Areas) (stations 8, 9, 10 and 11).

Table 1 Sampling locations in estuaries and port areas along the coastal marine areas of Tanzania.

Site	Location	Station	Coordinates
NCMA's	TPA (Tanga Port Area)	1	5°1.43' S, 39°5.16' E
	PRE (Pangani River Estuary)	2	5°25.46' S, 38°58.01' E
	WRE (Wami River Estuary)	3	6°7.17' S, 38°48.53' E
	RRE (Ruvu River Estuary)	4	6°24.03' S, 38°52.02' E
CCMA's	MRE (Msimbazi River Estuary)	5	6°47.50' S, 39°16.54' E
	DPA (Dar es Salaam Port Area)	6	6°51.32' S, 39°17.49' E
	MZC (Mzinga Creek)	7	6°52.19' S, 39°17.21' E
	RRE (Rufiji River Estuary)	8	7°44.32' S, 39°19.11' E
SCMA's	MAE (Matandu River Estuary)	9	8°43.26' S, 39°21.41' E
	MPA (Mtwara Port Area),	10	10°16.18' S, 40°11.13' E
	RVE (Ruvuma River Estuary)	11	10°29.35' S, 40°24.58' E

2.3 Collection of Biota Samples

Biota samples were collected from eleven sampling stations along the coastal marine area of Tanzania (Fig. 1). At each station, different species of macroalgae and seagrass were collected (hand-picked) for heavy metals analysis.

Prawns and shrimps were captured during low tide with a 12-mm mesh seine net, while gastropods and crabs were also hand-picked. These macrobenthos collected from the subtidal or intertidal areas were transported to the laboratory where they were identified using procedure of Richmond, M. D. [33]. The molluscs (gastropods and bivalves) and crustaceans (crabs and shrimps) from *A. dussumieri* and *L. lentjan* food chains were dissected from their exoskeleton or shells (using dissecting kits) prior to freeze-drying. Macrobenthos tissues were freeze dried for 3 days at -60 °C and grounded into powder using a mortar and pestle.

Samples of the catfish, the emperor and some other fish were purchased from fishers in the sampling sites. Most of the fish were caught by using hook and line and some by gill netting in the estuaries and port areas. Small fish were collected along with macrobenthos using a 12-mm mesh seine net. The collected fish were counted, weighed and identified using procedure of Bianchi, G. [34] and Richmond, M. D. [33]. Total length of each fish was measured to the nearest centimeter and their wet weight established. Muscle

tissue was taken from each fish for heavy metals analysis.

For stable isotopes analysis, the tissues were freeze-dried to constant weight for three days at -60 °C and homogenized by grinding into powder using agate mortar and pestle. Using the catfish *A. dussumieri* and the emperor *L. lentjan* as examples of higher trophic consumer, all organisms that were found to be part of their food web (as deduced from the gut content analysis results) were selected for isotopic analyses from all sampling sites. The same organisms were analysed for heavy metal accumulation.

2.4 Sample Digestion and Analysis of Heavy Metals (Laboratory Analyses)

The homogenized powder of the freeze dried biota was accurately weighed (0.5 g) and digested with 5 mL of concentrated HNO₃ for 1 hour at room temperature in a Teflon beaker (covered with watch glass). The samples were then heated at 80 °C on hot plate for 4 hours. The solution was then allowed to evaporate to 2.5 mL and cooled and diluted to 50 mL with Mill-Q water [35]. The analysis of As, Hg, Cd, Cr and Zn in the samples was performed on an ICP-OES (Inductively Coupled Plasma—Optical Emission Spectroscopy), Horiba Jobin Yvon, Ultima 2 at the SEAMIC (Southern and Eastern African Mineral Centre), Dar es Salaam. The instrument was calibrated using relevant standards (Merck, Germany).

Analytical blanks were run in the similar way as that of the samples and the concentrations were determined using the standard solutions prepared in the same acid matrix. The concentration of metals in biota is expressed in dry weight basis ($\mu\text{g/g d.w.}$).

2.5 Quality Control

The accuracy of the method was checked by analysing certified reference material DORM-2 (dogfish muscle) from the National Research Council of Canada. The accuracy of the determination of heavy metals in the DORM-2 was good; it ranged from 95% to 99% (Table 2).

2.6 Statistical Analysis

Statistical analyses were performed using SPSS 16.0 for Windows, Microsoft excel and PRIMER 6. Results of the heavy metal analyses in biota were subjected to a one-way ANOVA (Analysis of Variance) to test for significant differences ($p = 0.05$) in the concentrations of the heavy metals in the tissues of the different species of biota at different sampling sites. The overall consumer isotope signatures ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) among sites were tested by Pearson rank correlation and linear regression analysis with the concentration of heavy metals. Heavy metals concentrations were $\log_{10}$ -transformed to reduce the differences and kurtosis of the raw data prior to statistical analysis.

3. Results

3.1 Heavy Metal Concentrations in Biota Samples

3.1.1 Arsenic

The mean concentration of As in macroalgae was highest ($4.10 \pm 1.51 \mu\text{g/g}$) in samples from NCMA (stations 1, 2, 3 and 4) of Tanzania in comparison with

($2.27 \pm 0.61 \mu\text{g/g}$) in samples from CCMA (stations 5, 6 and 7) of Tanzania. The lowest concentration ($0.30 \pm 0.01 \mu\text{g/g}$) was in samples from the SCMA (stations 8, 9, 10 and 11) of Tanzania (Fig. 2). There was significant difference (ANOVA $p < 0.05$, $F = 1.023$) between As concentration in macroalgae from the three coastal locations (Table 3). The maximum concentration of As ($8.30 \pm 1.91 \mu\text{g/g}$) was measured in *S. asperifolium* from Ruvu river estuary (station 4), while the lowest concentration ($0.10 \pm 0.01 \mu\text{g/g}$) was reported in the *Chaetomorpha sp.* also from Ruvuma river estuary (station 11).

The results show that, bivalves from the CCMA had relatively higher concentrations of As ($3.17 \pm 1.22 \mu\text{g/g}$) as compared to $2.88 \pm 1.02 \mu\text{g/g}$ and $1.87 \pm 0.14 \mu\text{g/g}$ measured from SCMA and NCMA respectively (Fig. 3). There was significant difference (ANOVA $p < 0.05$, $F = 5.935$) in As contents in molluscan bivalves collected from the three coastal marine areas (Table 3). Higher concentration of As ($4.00 \pm 0.02 \mu\text{g/g}$) was found in *A. arcuatula* from Dar es Salaam port area and *Crassostrea sp.* from Ruvuma river estuary, while the lowest concentration ($1.00 \pm 0.12 \mu\text{g/g}$) was measured in *Crassostrea sp.* from Tanga port area (Fig. 3). Significantly (ANOVA, $p > 0.05$, $F = 0.457$) higher concentrations of As ($2.25 \pm 0.18 \mu\text{g/g}$) were measured in crustaceans from the NCMA while levels found in samples from CCMA and SCMA were $2.08 \pm 0.36 \mu\text{g/g}$ and $1.94 \pm 0.19 \mu\text{g/g}$ respectively (Fig. 4). The highest concentration of As ($4.00 \pm 1.11 \mu\text{g/g}$) was measured in the shrimp *P. indicus* from Msimbazi river estuary, while the lowest concentration ($0.50 \pm 0.02 \mu\text{g/g}$) was found in the crab *P. pelagicus* from Matandu river estuary (Fig. 4).

Levels of As recorded in fish species from the CCMA was relatively higher ($3.40 \pm 1.03 \mu\text{g/g}$)

Table 2 Mean ($\pm$ SD) concentration of metals ($\mu\text{g/g}$) in the certified reference material DORM-2 (SD: Standard Deviation).

	As	Hg	Cr	Pb	Zn
Certified	18 ± 1.7	4.64 ± 0.26	34.7 ± 5.5	0.065 ± 0.007	25.6 ± 2.3
Observed	17.5 ± 3.2	4.43 ± 0.27	34.4 ± 3.2	0.062 ± 0.009	25.3 ± 1.9
% recovery	97.2	95.4	99.1	95.5	98.8

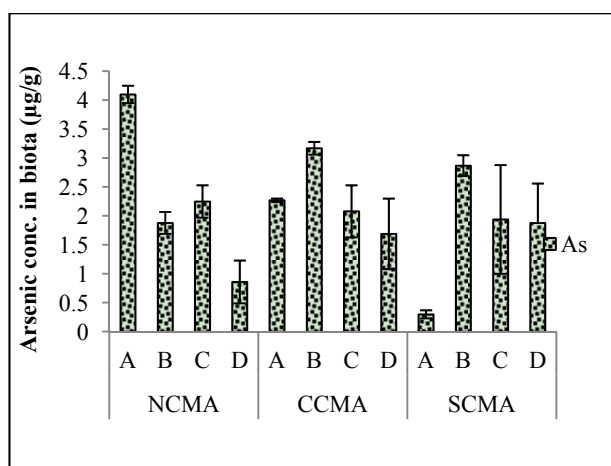


Fig. 2 Concentration (mean $\pm$ SD) of As in biota samples (A = macroalgae; B = bivalves; C = crustaceans; D = fish) from the NCMA, the CCMA and the SCMA.

compared to 2.08 ± 0.97 $\mu\text{g/g}$ and 0.62 ± 0.14 $\mu\text{g/g}$ in fish species from SCMA and NCMA respectively (Fig. 5). As content (7.80 ± 2.03 $\mu\text{g/g}$) found in the zoobenthivorous fish *P. quadrilineatus* from Mtwara

port area (station 10) was significantly higher than concentrations measured in the omnivorous fish *A. dussumieri* (0.10 ± 0.04 $\mu\text{g/g}$) from Matandu river estuary (ANOVA $p < 0.05$, $F = 0.583$) (Table 3). As concentrations in fish were compared with quality guidelines values FAO (Food and Agricultural Organization) [36] and they all were below permissible limits of 1.4 $\mu\text{g/g}$ w.w. (Table 4).

3.1.2 Mercury

The mean concentration of mercury in macroalgae samples was almost similar (0.03 ± 0.01 $\mu\text{g/g}$) in samples from SCMA, NCMA and CCMA. There was significant difference (ANOVA $p < 0.05$, $F = 1.286$) in Hg concentration in macroalgae from the three coastal marine areas of Tanzania (Table 3). The maximum concentration of Hg (0.06 ± 0.03 $\mu\text{g/g}$) was found in the *U. fasciata* from Msimbazi river estuary, while the lowest concentration of the metal ($0.01 \pm$

Table 3 ANOVA, heavy metal concentrations in macroalgae, macrobenthos, crustaceans and fish samples.

	Sum of squares	Df *	Mean square	F	Sig.
Macroalgae					
As	38.031	7	5.433	1.023	0.544
Hg	0.002	7	0	1.286	0.457
Cr	1,774.511	7	253.502	5.778	0.089
Pb	10.259	7	1.466	0.402	0.855
Zn	13,789.41	7	1,969.916	0.28	0.925
Bivalves					
As	10.386	7	1.484	5.935	0.086
Hg	0.001	7	0	1.223	0.476
Cr	354.784	7	50.683	2.153	0.284
Pb	1,787.67	7	255.381	3.201	0.184
Zn	1,054,670	7	150,667.1	4.631	0.118
Crustaceans					
As	5.818	10	0.582	0.457	0.886
Hg	0	10	0	0.189	0.993
Cr	41.25	10	4.125	9.811	0
Pb	2.704	10	0.27	1.565	0.237
Zn	119,718.8	10	11,971.88	2.428	0.081
Fish					
As	111.747	26	4.298	0.583	0.843
Hg	0.018	26	0.001	3.844	0.05
Cr	594.492	26	22.865	0.323	0.98
Pb	90.464	26	3.479	11.134	0.003
Zn	420,978.8	26	16,191.49	149.202	0

*Df: degree of freedom.

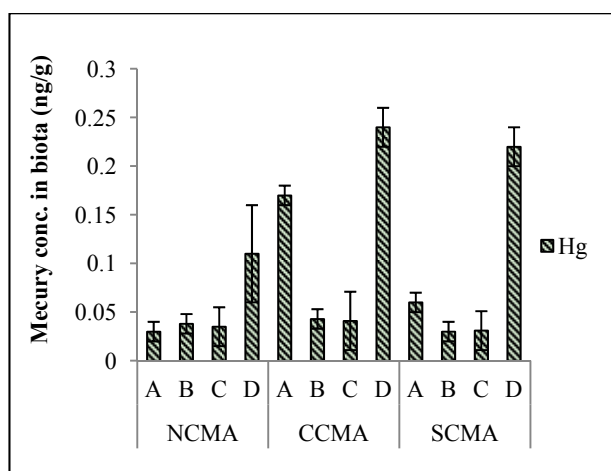


Fig. 3 Concentration (mean $\pm$ SD) of Hg in A = macroalgae; B = bivalves; C = crustaceans; and D = fish from the NCMA, CCMA and SCMA.

Table 4 The average concentrations of trace metals in fish as recommended by the FAO [36].

Specie	Unit	Pb	Zn	Cr	Hg	As
Fish	$\mu\text{g/g w.w.}$	2	50	1	0.5	1.4

0.00 $\mu\text{g/g}$) was found in the *U. petrusa* from the Dar es Salaam port area (Fig. 2). Bivalves from the CCMA had relatively higher concentrations of Hg ($0.04 \pm 0.02 \mu\text{g/g}$) compared to the concentration ($0.04 \pm 0.01 \mu\text{g/g}$) in NCMA and concentration ($0.03 \pm 0.01 \mu\text{g/g}$) in SCMA. There was significant difference (ANOVA $p < 0.05$, $F = 1.223$) in Hg contents in bivalves collected from the three main coastal locations (Table 3). The highest concentration of Hg ($0.06 \pm 0.03 \mu\text{g/g}$) was found in *A. arcuatula* from Mzingu Creek, while the lowest concentration ($0.02 \pm 0.01 \mu\text{g/g}$) was found in *Crassostrea sp.* from Ruvuma river estuary (Fig. 3).

The results show that crustaceans from the CCMA had almost similar concentrations of Hg ($0.04 \pm 0.02 \mu\text{g/g}$) with NCMA. Lower concentration ($0.03 \pm 0.01 \mu\text{g/g}$) was found in SCMA. There was significant difference (ANOVA $p < 0.05$, $F = 0.189$) in Hg contents in crustaceans collected from the three coastal locations (Table 3). Higher concentration of Hg ($0.05 \pm 0.03 \mu\text{g/g}$) was found in the crab *P. pelagicus* from Dar es Salaam port and Tanga port areas and in the crab *S. serrata* from the estuaries of

Wami and Ruvu rivers. Lower concentration of Hg ($0.02 \pm 0.01 \mu\text{g/g}$) was found in the shrimp *P. indicus* from stations 1, 3, 7, 10 and 11 (Fig. 4). Like crustaceans, fish species from CCMA had almost similar concentrations of Hg ($0.05 \pm 0.03 \mu\text{g/g}$) as those from SCMA ($0.05 \pm 0.02 \mu\text{g/g}$). The lower concentration ($0.04 \pm 0.01 \mu\text{g/g}$) was reported in NCMA (Fig. 4). There was significant difference (ANOVA $p < 0.05$, $F = 3.844$) in Hg contents in the fish species collected from the three coastal locations (Table 3). Higher concentration of Hg ($0.08 \pm 0.03 \mu\text{g/g}$) was found in the carnivorous fish *L. lentjan* from Msimbazi river estuary and also in the tissues of an omnivorous fish *A. dussumieri* from Matandu river estuary (Fig. 5). The lowest concentration ($0.01 \pm 0.00 \mu\text{g/g}$) was found in the herbivorous fish *S. ghobban* from Tanga port area, planktivorous fish *H. kelee* from Ruvu river estuary, planktivorous fish *S. albella* from Matandu river estuary and in the detritivorous fish *V. seheli* from Ruvuma river estuary (Fig. 4). Hg concentrations in fish were compared with quality guidelines values FAO [36] and they all were below permissible limits of $0.5 \mu\text{g/g w.w.}$ (Table 4).

3.1.3 Chromium

The highest concentration of chromium was found in the macroalgae samples ($23.67 \pm 8.19 \mu\text{g/g}$) from the CCMA of Tanzania. An intermediate concentration ($12.00 \pm 4.56 \mu\text{g/g}$) was found in the NCMA of Tanzania, while lowest concentration ($3.75 \pm 1.81 \mu\text{g/g}$) was found in the samples from the SCMA of Tanzania (Fig. 3). These concentrations were statistically different across the three coastal locations (ANOVA, $p < 0.05$, $F = 5.778$) (Table 3). The maximum concentration of Cr ($45.50 \pm 6.38 \mu\text{g/g}$) was found in the *U. petrusa* from Dar es Salaam port area, while the lowest concentration ($2.00 \pm 0.03 \mu\text{g/g}$) was found in the *Chaetomorpha sp.* from Ruvuma river estuary (Fig. 2). The bivalves from the NCMA had relatively higher concentration of Cr ($11.13 \pm 5.25 \mu\text{g/g}$) compared to $7.40 \pm 2.14 \mu\text{g/g}$ and $5.00 \pm 1.01 \mu\text{g/g}$ recorded in from SCMA and CCMA

respectively (Fig. 3). Although there was significant difference in mean Cr contents in molluscan bivalves collected from the three coastal locations (ANOVA, $p < 0.05$, $F = 2.153$), within site comparison revealed that higher concentration ($21.00 \pm 9.19 \mu\text{g/g}$) was found in *S. cuculata* from Mtwara port area while lower concentrations ($2.00 \pm 0.42 \mu\text{g/g}$) were found in the tissues of the *A. arcuatula* and *Crassostrea sp.* from Mzinga Creek and Ruvuma river estuaries respectively (Fig. 3 and Table 3). Crustaceans from the SCMAs had relatively higher concentrations of Cr ($3.10 \pm 0.88 \mu\text{g/g}$) compared to $3.00 \pm 1.14 \mu\text{g/g}$ in samples from CCMA and $2.25 \pm 1.33 \mu\text{g/g}$ in samples from NCMA. There was no significant difference (ANOVA $p > 0.05$) in Cr contents in crustaceans collected from the three coastal marine areas (Table 3). The highest concentration of Cr ($8.00 \pm 3.17 \mu\text{g/g}$) was found in the shrimp *P. indicus* from Mtwara port area, while the lowest concentration ($1.00 \pm 0.02 \mu\text{g/g}$) was found in the crab *S. serrata* from Rufiji river estuary (Fig. 4). Results further elucidate that fish species from the NCMA accumulated relatively higher Cr ($5.50 \pm 0.19 \mu\text{g/g}$) compared to values recorded in fish species from CCMA ($4.80 \pm 0.61 \mu\text{g/g}$) and SCMA ($2.30 \pm 0.13 \mu\text{g/g}$). There was significant difference in Cr contents in the fish species collected from the three coastal locations (ANOVA $p < 0.05$, $F = 0.323$) (Table 3). The highest concentration of Cr ($14.50 \pm 5.13 \mu\text{g/g}$) was found in the carnivorous fish *L. lentjan* collected from Mzinga Creek, while the lowest concentration ($1.00 \pm 0.02 \mu\text{g/g}$) was found in the detritivorous fish *L. macrolepis* from Rufiji river estuary and herbivorous fish *S. sutor* from Dar es Salaam port area (Fig. 5). Cr concentrations in fish were compared with quality guidelines values FAO [36] and they all were below permissible limits of $1.0 \mu\text{g/g w.w.}$ (Table 4).

3.1.4 Lead

The mean concentration of lead in macroalgae samples was highest ($2.75 \pm 0.52 \mu\text{g/g}$) in samples from the NCMA of Tanzania, followed by the

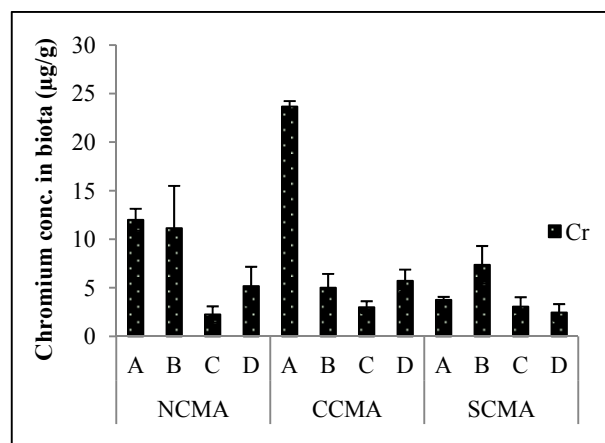


Fig. 4 Concentration (mean $\pm$ SD) of Cr in A = macroalgae; B = bivalves; C = crustaceans; and D = fish from NCMA, CCMA and SCMA.

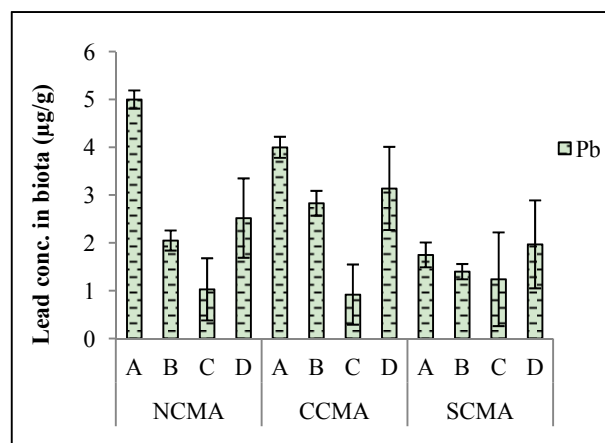


Fig. 5 Concentration (mean $\pm$ SD) of Pb in A = macroalgae; B = bivalves; C = crustaceans; and D = fish from NCMA, CCMA and SCMA.

CCMA ($1.37 \pm 0.18 \mu\text{g/g}$) and $1.15 \pm 0.26 \mu\text{g/g}$ in samples from the SCMA of Tanzania (Fig. 2). Significant difference existed in mean Pb concentrations of macroalgae samples collected from the three coastal locations (ANOVA $p < 0.05$, $F = 0.402$), (Table 3). Maximum concentration of Pb ($5.50 \pm 1.08 \mu\text{g/g}$) was found in *S. asperifolium* from Ruvu river estuary, while the minimum concentration of the metal ($0.10 \pm 0.02 \mu\text{g/g}$) was measured in the *U. petrusa* from Dar es Salaam port area. The results also show that bivalves from the CCMA had relatively higher concentrations of Pb ($2.83 \pm 0.86 \mu\text{g/g}$) compared to bivalves from NCMA ($2.05 \pm 0.93 \mu\text{g/g}$) and SCMA ($1.40 \pm 0.65 \mu\text{g/g}$). Significant difference

was found in Pb contents in molluscan bivalves across the three coastal locations (ANOVA $p < 0.05$, $F = 3.201$). Highest concentration of Pb ($5.00 \pm 1.17 \mu\text{g/g}$) was found in *Crassostrea sp.* from Pangani river estuary and lower values ($0.50 \pm 0.02 \mu\text{g/g}$) was measured in *Crassostrea sp.* from Tanga port area (Fig. 5). Crustaceans from the SCMAS had relatively higher concentrations of Pb ($1.24 \pm 0.52 \mu\text{g/g}$) compared to crustaceans collected from NCMA (1.03 $\pm 0.46 \mu\text{g/g}$) and CCMA (0.92 $\pm 0.31 \mu\text{g/g}$) (Fig. 3). Statistical results revealed significant difference in Pb content of crustacean tissues across the three sampled coastal marine areas (ANOVA $p < 0.05$, $F = 1.565$). Higher concentration of Pb ($1.80 \pm 0.39 \mu\text{g/g}$) was measured in the crab *P. pelagicus* from Ruvuma river estuary while the shrimp *P. indicus* from Wami river estuary, Ruvuma river estuary and Mtwara port area; and the crab *S. serrata* from Wami river estuary and *P. pelagicus* from Mzinga Creek recorded lower concentration ($0.50 \pm 0.02 \mu\text{g/g}$) of lead (Fig. 4). Results further reveal that fish species from the CCMA had relatively higher average concentrations of Pb ($2.60 \pm 1.32 \mu\text{g/g}$) compared to $2.33 \pm 0.98 \mu\text{g/g}$ from SCMA and $2.29 \pm 1.05 \mu\text{g/g}$ from NCMA. These results were statistically significant different across the three coastal marine locations (ANOVA $p < 0.05$, $F = 11.134$). The highest concentration of Pb ($8.00 \pm 3.07 \mu\text{g/g}$) was measured in the carnivorous *L. lentjan* from Dar es Salaam port area, while the lowest concentration ($0.50 \pm 0.12 \mu\text{g/g}$) was found in the herbivorous *S. ghobban* from Tanga port area, the planktivorous *S. albella* from the estuaries of Wami and Ruvu rivers, the detritivorous *L. macrolepis* and *V. seheli* from the estuaries of Rufiji and Ruvuma rivers respectively (Fig. 5). Pb concentrations in fish were compared with quality guidelines values FAO [36] and they all were below permissible limits of $2.0 \mu\text{g/g}$ w.w. (Table 4).

3.1.5 Zinc

The average concentration of zinc in macroalgae samples was highest ($111.50 \pm 5.17 \mu\text{g/g}$) in samples

from NCMA followed by SCMA ($60.63 \pm 3.53 \mu\text{g/g}$) and $51.00 \pm 1.26 \mu\text{g/g}$ in samples from CCMA. These results illustrate similar distribution of this metal across the three coastal marine areas (ANOVA $p < 0.05$, $F = 0.280$) (Table 3). Inter-site comparison show that highest concentration of Zn ($216.00 \pm 11.66 \mu\text{g/g}$) was found in *S. asperifolium* from Ruvu river estuary, while the lowest concentration ($23.50 \pm 8.93 \mu\text{g/g}$) was measured in the *U. fasciata* from Pangani river estuary (Fig. 2). The bivalves from the CCMA recorded higher concentrations of Zn ($616.50 \pm 21.14 \mu\text{g/g}$) compared to $167.30 \pm 16.85 \mu\text{g/g}$ from NCMA and $116.1 \pm 18.22 \mu\text{g/g}$ from SCMA. There was no significant difference (ANOVA $p > 0.05$, $F = 4.631$) in Zn contents in molluscan bivalves collected from the three coastal locations (Table 3). The highest concentration of Zn ($651.00 \pm 6.51 \mu\text{g/g}$) was measured in *Crassostrea sp.* from Msimbazi river estuary, while the lowest concentration ($29.50 \pm 7.93 \mu\text{g/g}$) was found in *S. cucullata* from Mtwara port area (Fig. 3).

Crustaceans from the NCMA had relatively higher concentrations of Zn ($165.90 \pm 33.39 \mu\text{g/g}$) compared to the concentration ($65.10 \pm 15.16 \mu\text{g/g}$) in CCMA and the lowest concentration ($52.00 \pm 22.16 \mu\text{g/g}$) in samples from SCMA. There was significant difference (ANOVA $p < 0.05$, $F = 2.428$) in Zn content in crustaceans collected from the three coastal locations (Table 2). The highest concentration of Zn ($411.50 \pm 13.04 \mu\text{g/g}$) was found in the crab *P. pelagicus* from Pangani river estuary, while the lowest concentration ($28.00 \pm 4.34 \mu\text{g/g}$) was measured in the shrimp *P. indicus* from Mtwara port area (Fig. 4). The results show that fish species from the SCMA had higher mean concentration of Zn ($101.10 \pm 21.16 \mu\text{g/g}$) compared to NCMA ($84.00 \pm 15.03 \mu\text{g/g}$) and CCMA ($61.40 \pm 19.82 \mu\text{g/g}$). There was no significant difference (ANOVA $p > 0.05$) in mean Zn contents in the fish species collected from the three coastal marine areas (Table 3). The highest concentration of Zn ($667.00 \pm 43.11 \mu\text{g/g}$) was measured in the omnivorous

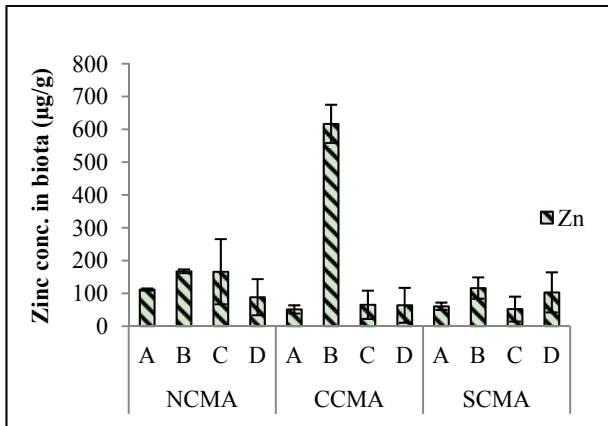


Fig. 6 Concentration (mean $\pm$ SD) of Zn in A = macroalgae; B = bivalves; C = crustaceans; and D = fish from NCMA, CCMA and SCMA.

fish *A. dussumieri* from Matandu river estuary, while the lowest concentration (17.00 ± 9.48 µg/g) was found in the zoobenthivorous fish *P. quadrilineatus* from Mtwara port area (Fig. 6). Zn concentrations in fish were compared with quality guidelines values FAO [36] and they all were below permissible limits of 50.0 µg/g w.w. (Table 4).

3.2 The TPs of *A. dussumieri* and *L. lentjan*

The estimation of the positions of the cat fish *A. dussumieri* and the emperor *L. lentjan* in the estuarine and nearshore waters of Tanzania was made using the stable C and N isotope results. The TP of fishes (TP_{SIA}), was calculated following the procedure of Cabana, G. and Rasmussen, J. B. [37] using Eq. (1):

$$TP_{SIA} = \left[\left(\text{Fish } \delta^{15}N - \text{Primary consumer } \delta^{15}N \right) / 3.4 \right] + 2 \quad (1)$$

Primary consumer $\delta^{15}N$ was calculated as the mean $\delta^{15}N$ of all primary consumers (i.e., filter feeder, collector, gatherer, shredder and grazer taxa) collected for a sampling event. Trophic guilds were assigned using the literature [38]. Stomach contents analysis also enabled the determination of TP of *A. dussumieri* and *L. lentjan*. By using gut content analysis, the TP of fish (TP_{GCA}) was also calculated according to the method of Vander-Zanden, M. J., et al. [39] using Eq. (2):

$$TP_{GCA} = \sum (P_i * T_i) \quad (2)$$

Where P_i is proportion of the i^{th} food item and T_i is TP of each food item. TPs of food items were based on literature dietary data [39, 40]. According to Lopez-Fernandez, H. and Winemiller, K. O. [38], in marine systems there are: algae at the bottom of the food web (TL = 1, by definition); herbivorous zooplankton feeding on the algae (TL = 2); large zooplankton or small fishes, feeding on the herbivorous zooplankton (TL = 3); large fishes (for example, cod, tuna and groupers) whose food tends to be a mixture of low-TP and high-TP organisms (TL = 3.5-4.5).

The stable nitrogen isotopic signatures results show that *A. dussumieri* and *L. lentjan* from all sampling stations belong to the TL of the secondary consumers. The estimated TP based on the stable isotopes of carbon and nitrogen based on the procedure of Cabana, G. and Rasmussen, J. B. [37] for *A. dussumieri* was 3.5 and that of *L. Lentjan* was 3.0. Individuals of *A. dussumieri* and *L. lentjan* increased in weight linearly, as their length increased. These findings are in agreement with the TP of marine fishes as estimated using $\delta^{15}N$ values [41]. Cabana, G. and Rasmussen, J. B. [37] reported a linear relationship between the size of individuals of benthic assemblages and their stable nitrogen isotope values. The good agreement between the determination of the TLs of 3.5 and 3.0 for *A. dussumieri* (Fig. 7) and *L. lentjan* (Fig. 8) respectively by using $\delta^{15}N$ method and the traditional approach of using the gut-content analysis supports the application of an average trophic enrichment of 3.4‰ between successive TL in the estimation of TPs of consumers as suggested by Vander-Zanden, M. J. and Rasmussen, J. B. [42].

3.3 Trophic Transfer of Heavy Metals along the Food Chains

The stable isotopes of C and N ($\delta^{13}C$ and $\delta^{15}N$) for the *A. dussumieri* and *L. lentjan* and their TLs were used in the investigation of trophic transfers of heavy metals along their food chains.

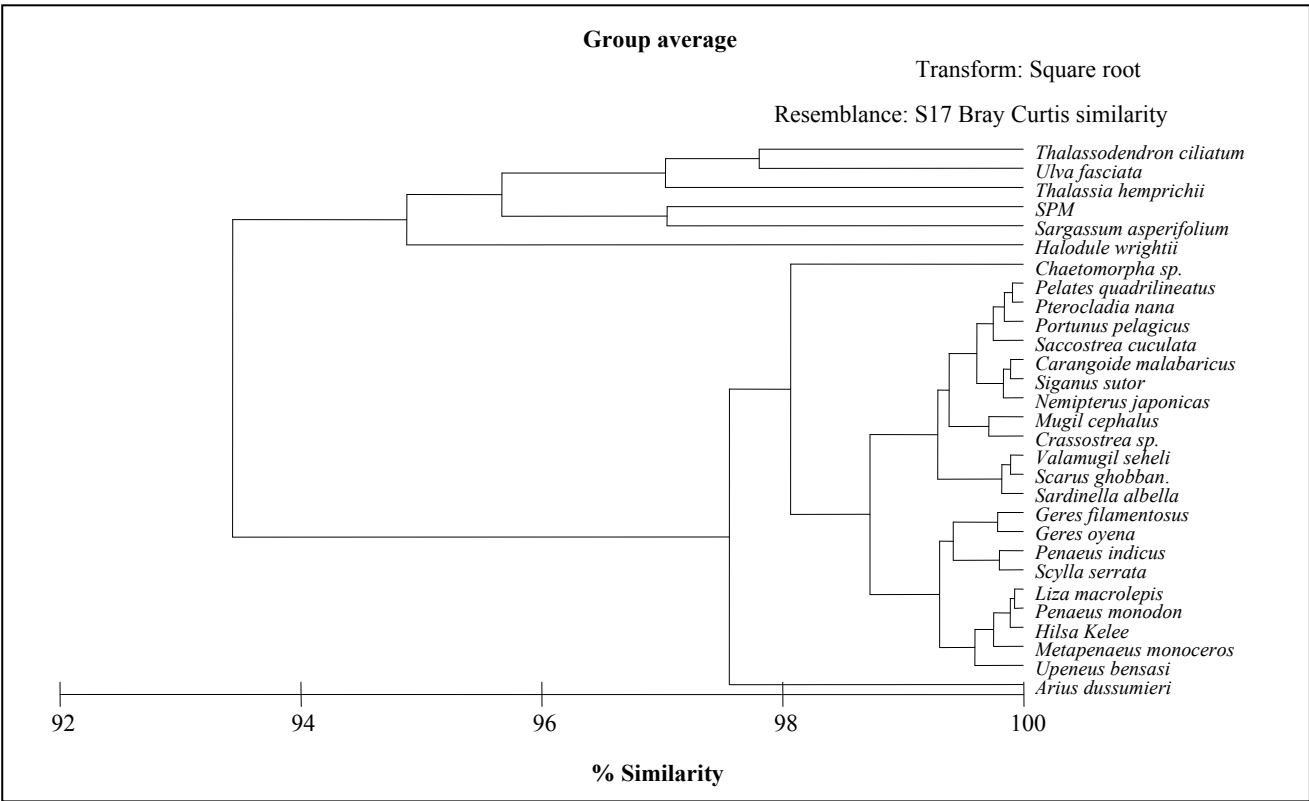


Fig. 7 Relationship between $\delta^{15}\text{N}$ and log-transformed Hg concentration in fish from Tanzanian coastal marine environment.

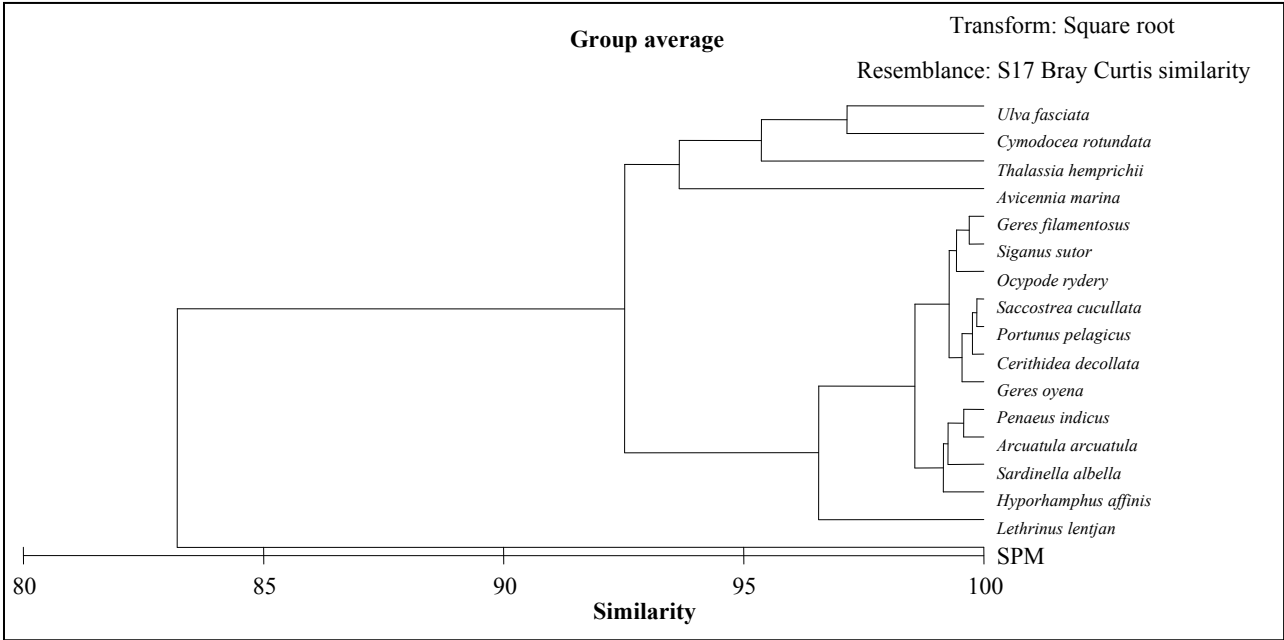


Fig. 8 Relationship between $\delta^{15}\text{N}$ and log-transformed Pb concentration in fish from Tanzanian coastal marine environment.

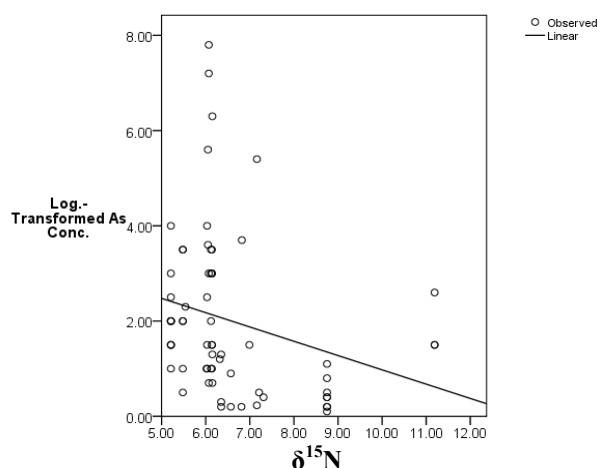


Fig. 9 Relationship between $\delta^{15}\text{N}$ and log-transformed As concentration in fish from Tanzanian coastal marine environment.

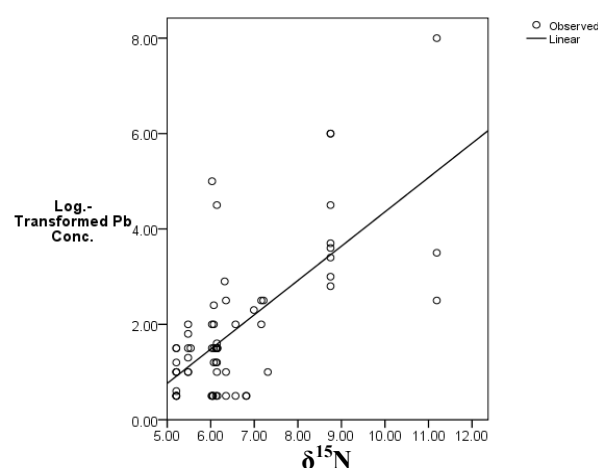


Fig. 12 Relationship between $\delta^{15}\text{N}$ and log-transformed Pb concentration in fish from Tanzanian coastal marine environment.

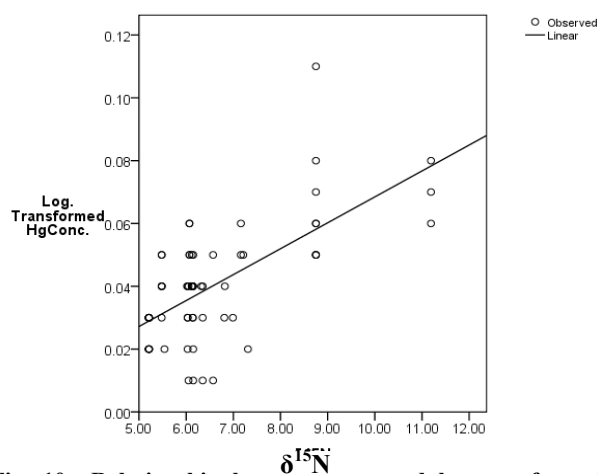


Fig. 10 Relationship between $\delta^{15}\text{N}$ and log-transformed Hg concentration in fish from Tanzanian coastal marine environment.

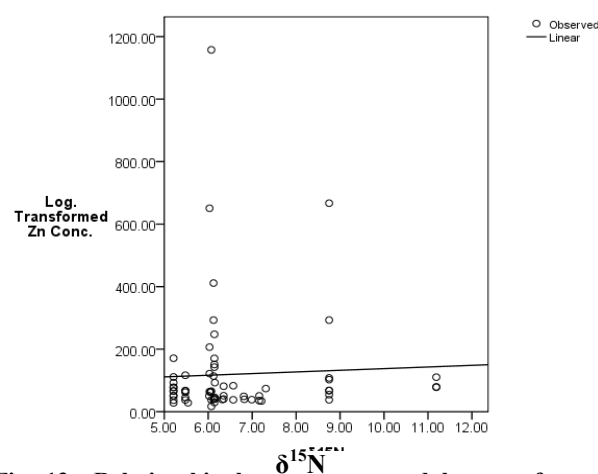


Fig. 13 Relationship between $\delta^{15}\text{N}$ and log-transformed Zn concentration in fish from Tanzanian coastal marine environment.

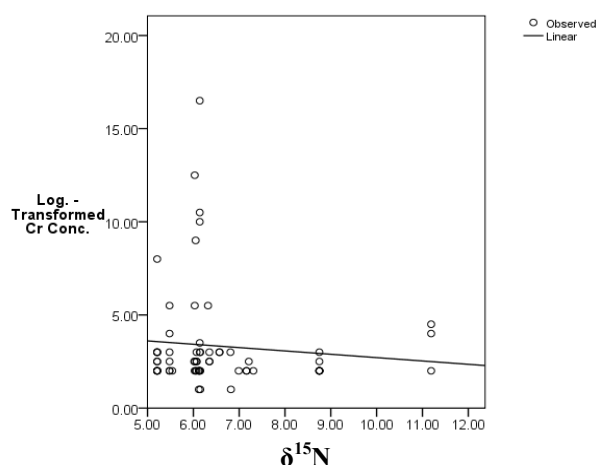


Fig. 11 Relationship between $\delta^{15}\text{N}$ and log-transformed Cr concentration in fish from Tanzanian coastal marine environment.

In the *A. dussumieri* and *L. lentjan* food chains, log concentrations of mercury and lead in muscle and soft tissues of animal samples were found to increase significantly ($p = 0.05$ and $p = 0.01$) with increasing TLs (Figs. 9 and 10). The slopes for these elements were 0.368 for log-transformed Hg and 0.246 for log-transformed Pb. Regressions for log As and Cr were significant, with a negative slope of -0.068 and -0.005 respectively (Figs. 11 and 12). Non-significant slope was found for Zn, indicating that this element neither biomagnifies nor biodilutes through the food web (Fig. 13).

There was a linear relationship between

log-transformed Hg and Pb concentrations with $\delta^{15}\text{N}$ values for biota analysed. The slope of regression line was negative between log-transformed As and Cr concentrations with $\delta^{15}\text{N}$ values, while completely flat regression line was between log-transformed Zn concentration with $\delta^{15}\text{N}$ values for biota. The steeper slope was observed between log-transformed Hg with $\delta^{15}\text{N}$ in biota as compared to the slope for Pb.

4. Discussion

4.1 Accumulation and Biomagnification of Heavy Metals along Food Chains of *A. dussumieri* and *L. lentjan*

4.1.1 Arsenic

Bioaccumulation of As was high in macroalgae from NCMAs followed by SCMAS and the last was CCMAs. Although As was not detected in the water samples, it was found to bioaccumulate in the three species of macroalgae. The significant BCF for As in the macroalgae *S. asperifolium* in Ruvu river estuary and *U. fasciata* in Msimbazi Creek was expected because of the high concentration of the As in the sediments from the stations. Higher BCF for As in *U. fasciata* from Wami river estuary could be due to high ability of *Ulva* sp. to accumulate arsenic from the environment as compared to other species of macroalgae in other stations. This idea is complemented by discussion given by Thomson, D., et al. [43] who reported that arsenic concentration and which are important primary producer in marine food chains. Rahman, M. A., et al. [44] reported that total arsenic concentrations varied between classes of algae, and significant differences between algae classes and habitats were found for the proportion of As species.

Bioaccumulation of arsenic in bivalves was generally low. The only significant BAF was found in *S. cucullata* in Mtwara port area (BAF = 133) in SCMAS. The results show that no significant BAF was found in crustaceans from NCMAs, CCMAs and also from SCMAS. The findings are in agreement with the previous report by Barwick, M. and Maher, W. [45]

which had reported that As and arsenic-containing organic compounds did not accumulate to a great extent in aquatic organisms due to its highly toxic nature.

The results on As bioaccumulation in fish showed that the metal had relatively high BAF in the fish from CCMAs, followed by SCMAS and then NCMAs. Only five fish species were found with significant BAF showing that they accumulate As from the environment. These fish species include the herbivorous *S. sutor* from Msimbazi river estuary (BAF = 108), the zoobenthivorous *P. quadrilineatus* from Mzinga Creek (BAF = 300), the omnivorous *A. dussumieri* from Mtwara port area (BAF = 183), and Wami river estuary (BAF = 133) as well as the zooplanktivorous *S. albella* also from Wami river estuary (BAF = 109). The high BAF for these fish suggests high availability of As at stations 3, 5 and 7. Hardersen, S. and Wratten, S. D. [46] reported in their research the uptake of As by fish from water, food, sediments and suspended particulate material. Therefore, arsenic present in both water and sediments at these sampling stations was available for uptake by fish. The uptake of sediment-associated contaminants by fish may occur by respiratory and dietary routes, whereas the dermal route is usually a minimal contributor of exposure, due to the often effective barrier provided by the external epithelium [47].

The result of trophic transfer (trophodynamics) of As along *A. dussumieri* and *L. lentjan* food chain is described by negative regression which means biodilution of the metal (Fig. 8). The finding was confirmed by the elevated concentrations of arsenic in the macroalgae, macrobenthos and small fish, while larger fish had lower concentrations. Interpretation of this observation is supported by the findings of Wang, W. X. [9] who reported that concentrations of metals decreased at a higher TL in the marine food chain. This is mainly a result of an effective efflux of metals from macrobenthos and a very low assimilation of metals by marine fish. Other researchers have reported

that arsenic and/or its metabolites is a chemical that bioaccumulates in tissues of aquatic organisms but does not biomagnify, rather it biodilutes in the aquatic food chain [31, 48-50]. Yet Thomson, D., et al [43] report that, dietary exposure to arsenic from aquatic foods would not be a serious problem for humans due to its biodiminution and biotransformation to less toxic organo-As species.

4.1.2 Mercury

Results show that bioconcentration of mercury were higher in the macroalgae from CMCA's followed by SCMA's and NCMA's. Bioaccumulation of mercury was higher in the macroalgae than in all other biota analysed, with significant BCFs measured in eight stations out of eleven. Higher significant BCF values were found in *U. fasciata* from Msimbazi river estuary (1,700), in *U. petrusa* from Dar es Salaam port area (700) and in *Chaetomorpha sp.* from Rufiji river estuary (900). These results show that *Ulva sp.* and *Chaetomorpha sp.* have a higher ability to accumulate Hg from the environment as compared to other macroalgae species. The high BCFs for macroalgae were also related to the sampling stations with higher concentrations of available Hg in water and sediments. Karez, C. S., et al. [51] reported that high levels of Hg in the algae reflect the high bioavailability of metals and the capacity of the algae to accumulate metals.

The macrobenthos (bivalves and crustaceans) had generally low BAFs throughout the study area suggesting that most of the macrobenthos accumulate heavy metals from biota they consume. Low BAFs values for this group of organisms could, therefore, be due the use of water and sediments data in computing BAFs. Similar results have been reported by Lee, B. G., et al. [52] that most benthic organisms obtain a large fraction of their contaminants through ingestion and not by direct accumulation from overlying water or pore-water. Similarly, the BAFs for mercury in fish from coastal marine area of Tanzania were low and not significant. These indicative results suggest that at present, fish in the coastal marine areas of Tanzania

are not bioaccumulating Hg from the environment. Low BAFs for Hg in fish are probably a result of the low concentration of available Hg in these environments. Romeo, M., et al. [53] observed that the ability of fish to accumulate heavy metals depended on ecological needs, metabolism, and the extent of pollution in sediment, water and food items.

Results on trophic transfer of Hg along *A. dussumieri* and *L. lentjan* food chains in this study show that biomagnification of Hg was evidenced by a positive regression results (Fig. 9). This was further confirmed by elevated Hg concentrations in the big fish, while small fish, macroalgae and macrobenthos had lower concentrations. Regression relationships between Hg concentrations and $\delta^{15}\text{N}$ have been discussed in other aquatic food chains [15, 29, 30, 54, 55] demonstrating biomagnification of mercury along food chains despite low ambient concentrations of this metal in the environment. Results of this study display similar mechanism of biomagnification of metals from lower TL organisms such as plankton or algae to higher TL organisms such as *A. dussumieri* and *L. lentjan* food webs.

Higher Log.-mercury slope found in this study compared to Log.-lead slope gives evidence that Hg is the major biomagnifying element in *A. dussumieri* and *L. lentjan* food chains from Tanzania coastal marine environment. This means that Hg is biomagnified through this food webs as evidenced by $\delta^{15}\text{N}$ regardless of productivity or salinity (marine vs. freshwater) of the ecosystem. This argument is supported by the results reported by Campbell, L. M., et al. [15] who found that MeHg measured by $\delta^{15}\text{N}$ is biomagnified through diverse food webs, regardless of productivity (eutrophic vs. oligotrophic), latitude (arctic vs. tropical) or salinity (marine vs. freshwater) of the ecosystem.

4.1.3 Chromium

The results show that the bioconcentration of chromium was higher in the macroalgae from CCMA's, followed by macroalgae from NCMA's and SCMA's.

Generally, chromium was found to significantly bioaccumulate in all the analysed species of macroalgae. Significant BCF values for Cr were found in the *U. petrusa* from Dar es Salaam port area (1,820) and in *U. fasciata* from Wami river estuary (1,240). The high BCFs for macroalgae are in agreement with the high Cr concentration that was observed in the water samples from the sampling stations. *Ulva sp.* had the highest ability to accumulate Cr as compared to the other species of macroalgae. The high BCFs are also indicative of the high dissolved Cr in water samples from Wami river estuary and Dar es Salaam port area. According to Luoma, S. N. [56], unlike other bioindicators of heavy metal contamination such as filter-feeding animals, macroalgae accumulate dissolved metal ions in the waters. Therefore, only heavy metals with high solubility products are expected to have significant BCFs in macroalgae.

The bivalves from NCMA had high BAFs for chromium, followed by SCMA and CCMA. Significant BAFs for Cr in bivalves were measured only in *S. cucullata* from Wami river estuary (220), Ruvu river estuary (111) and Mtwara port area (300). Similarly, water samples from CCMA were found to contain higher particulate chromium as well as higher percentage of available Cr in the sediment as compared to NCMA and SCMA. *S. cucullata* was found to have high ability to accumulate and store chromium in their tissues as compared to the ability of *A. arcuata*. This observation is in agreement with the research data from China in which *S. cucullata* were described as the strongest metal accumulators among bivalve species [57]. The accumulation of chromium by crustaceans from the coastal marine areas of Tanzania was low with no crustacean found having significant BAF. Similarly, there was a low bioaccumulation of Cr in fish from the studied locations with no fish having significant BAF. It can therefore be suggested that crustaceans and fish do not significantly bioaccumulate chromium from the environment (water and sediment).

The biomagnification results showed that there was a decrease of concentration of Cr along *A. dussumieri* and *L. lentjan* food chains (biodilution) which was implied by negative regressions graphs (Fig. 10). The result was further confirmed by the elevated concentrations of Cr in the macroalgae, macrobenthos and small fish, while larger fish had lower concentrations. It has been reported that concentrations of metals decrease at a higher TL in the marine food chain as a result of an effective efflux of metals from macrobenthos and a very low assimilation of metals by marine fish [9].

4.1.4 Lead

Lead is the only heavy metal which has no significant BCF in macroalgae from all the three main sites despite some high Pb concentrations in sediments from the study area. The low BCFs in the macroalgae are related to the low concentration of lead in the water samples which was largely below the detection limit. It is well known that macroalgae accumulate heavy metals proportional to the surrounding medium [58] and that the accumulation of the heavy metal such as Pb in macroalgae depends on the factors like metal contents in water, absorption properties of the algae species, and to some extent the metal content of sediment [59].

Bivalves *S. cucullata* from the estuaries of Rufiji and Matandu rivers (290 and 193, respectively) in SCMA had significant BAF for lead. Significant BAF was also found in *S. cucullata* from Wami river estuary (133) and Ruvu river estuary (141) in NCMA. Other bivalves displayed insignificant values for BAF of this metal. On the other hand, sediments from the estuaries of Wami, Ruvu, Rufiji and Matandu rivers had high concentration of available Pb which possibly has an influence on the observed BAFs. Insignificant BAFs displayed by crustaceans and fish are a clear indication that these species do not substantially bioaccumulate Pb from the coastal marine areas of Tanzania.

Positive regressions result elucidates that Pb biomagnifies along *A. dussumieri* and *L. lentjan* food

chains in Tanzanian coastal marine waters (Fig. 11). Elevated Pb concentrations in the big fish species relative to small fish, macroalgae and macrobenthos displaying lower concentrations of this metal in this study further confirm this observation. Positive regression relationships between $\log_{10}$ transformed Pb concentrations and $\delta^{15}\text{N}$ have been used by different authors in delecting biomagnification of this metal in aquatic food webs [12, 18, 29, 30]. In the present study, the graph (Fig. 11) of log-transformed Pb slope was lower than that of Hg indicating that Hg potentially biomagnifies more than Pb along *A. dussumieri* and *L. lentjan* food chains.

4.1.5 Zinc

The results show high BCF for zinc in macroalgae from the coastal marine areas of Tanzania. Highly significant BCF values were observed in *S. asperifolium* from Ruvu river estuary (3,323), in *Chaetomorpha sp.* from Ruvuma river estuary (1,536), *U. fasciata* from Matandu river estuary (1,164) and in *U. fasciata* from Wami river estuary (1,088). The high BCFs for macroalgae are consistent with the observed high zinc concentration in the macroalgae. The results also suggest that the macroalgae have a high ability of bioaccumulating zinc in the tissue.

The bioaccumulation of Zn was also high in bivalves from all sites. The significant BAFs were found in *A. arcuatula* from Mzinga Creek (1,630) and *S. cuculata* from the estuaries of Ruvu, Wami and Rufiji rivers (307, 204 and 187, respectively). The high values of BAFs relates well with the concentration of Zn in the suspended particulate matter which was higher at Mzinga Creek and Rufiji river estuary. Similarly, higher concentrations of available zinc in sediments were found at the estuaries of Msimbazi, Rufiji and Ruvu rivers. The current study argues that bivalves have high ability to accumulate zinc, and that molluscan life processes do not seem to be affected by excess zinc which is frequently accumulated far in excess of the organism's immediate needs [60].

The bioaccumulation of zinc in crustaceans from the coastal marine areas of Tanzania was high. The significant BAF was observed in the *P. indicus* and *P. pelagicus* from Mtwara port area, in *P. indicus* and *P. pelagicus* from Ruvuma river estuary and in *P. indicus* and *S. serrata* from Rufiji river estuary. However, there was no crustacean with significant BAF from NCMA's, probably due to the lower values of available Zn in the sediment from NCMA's. A study by Romeo, M., et al. [61] discusses that Zn can be taken up and accumulated in tissues and bodies of many species of marine invertebrates to concentrations usually much higher than concentrations in the surrounding seawater or sediments.

Only four fish species were found to accumulate zinc in their tissues to a significant extent from the coastal marine areas of Tanzania. The significant BAF was observed in the omnivorous *A. dussumieri* from the estuaries of Matandu, Ruvu and Wami rivers (733, 364 and 146, respectively) and Mtwara port area (143). The observed significant BAF of Zn in the catfish *A. dussumieri* from all sites was probably due to the feeding habit. Previous studies [62, 63] have reported that variability of levels of metals such as Zn in different fish species is a function of feeding habits, ecological needs, metabolism or age, size and length of the fish and their habitats, which affirms the argument.

Zinc trophodynamic results are explained by positive regression slope and confirmed by evenly distribution of Zn in macroalgae, macrobenthos and fish. The results clarify that Zn concentrations did not increase or decrease with TLs along *A. dussumieri* and *L. lentjan* food chains (Fig. 12). Zinc is an essential element with many important metabolic functions which necessitates most organisms to have biochemical mechanisms to regulate the amount of Zn in their cells [63]. Campbell, L. M., et al. [15], suggested that the rate of Zn excretion would be relative to Zn ingestion, thereby ensuring a relatively constant concentration in biota throughout the food web.

5. Conclusion

This study revealed evidently the slight biomagnification of heavy metals mercury (Hg) and lead (Pb) in fish tissues collected from the coastal marine areas of Tanzania. Therefore, a regular monitoring of heavy metal levels in fishes is necessary. Despite these observations, heavy metal levels in fish muscles in this study were generally below the permissible limits suggested by FAO [36] and posed no threat to public health yet.

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Evaluating Climate Change Effects on Natural Resources Using Remote Sensing Technologies: A Case of Kazimzumbwi Forest Reserve, Kisarawe in Tanzania

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Abstract: Poor countries are prone to climate change effects due to lack of mechanisms to mitigation. As such, they are most vulnerable to effects of climate changes which are floods, drought, deforestation, environmental degradation and so on. Many of affected communities particularly in rural areas and urban poor have resorted to migration to viable agricultural lands and urban areas increasing pressure on available social services. This situation has led to depletion of natural resources in the fringes of the cities in search for shelter, food, water, energy etc.. Dar es Salaam city is highly prone to environmental degradation by being highly populated and closer to the Kazimzumbwi Forest National Reserve, which has been a resource of logging at the guise of sustainable livelihood of Dar es Salaam city residents. This paper is reporting on a study undertaken in ENVI & ARCGIS software environment to evaluate the extent of environmental degradation in the forest reserve for the period of 16 years i.e. 1995-2011, firstly, for purpose of informing policy makers and administrators to determine the extent of the problem and secondly to provide evidence for development of effective mitigation measures. Results revealed a considerable environmental degradation within the forest reserve over the study period. This was attested by a decrease of forests by 42%, grass land, as well as increase of bare land and grass land by 26% and 42% respectively. This is a testimony that there was a significant environmental degradation and loss of natural resources during the study period which should be addressed by relevant authorities.

Key words: Climate change, environmental degradation, image classification, change detection.

1. Introduction

Climate change is a global phenomenon threatening livelihood of mankind; ironically it is caused by activities supporting mankind's existence and prosperity. The root cause of climate change is lack of natural balance of GHG (Green House Gases) effectively and CO₂ between the atmosphere and the earth. Whereas human activities such as deforestation, burning of fossil fuels from vehicles, plane travel, heavy industries are some of the activities which are acknowledged to catalyze climate change by emission of carbon dioxide; forests and vegetation in general

use carbon dioxide in photo synthesis and plant respiration.

As such, forests play a double role in the carbon dioxide equilibrium, firstly, as reservoirs of carbon dioxide from the atmosphere and secondly as generators of carbon dioxide when they are cut [1]. The major reservoirs of carbon include the oceans, the soils and the atmosphere. Carbon dioxide naturally, flows from one reservoir to another, over time, ranging from days to decades as noted by Pearson, T., et al. [2].

The carbon cycle helps to regulate the amount of CO₂ present in the atmosphere, and therefore a major component of climate system stability. Specifically, when fossil fuels are burnt, they upset the natural balance of GHG in the atmosphere, leading to

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depletion of ozone layer which protects the earth's surface from low wave length radiations e.g. ultraviolet radiation from the sun.

Burning of fossil fuels is also responsible for accumulation of other GHG e.g. methane which tends to tap longer wavelength radiations emitted from the earth's surface. Consequently, the earth receives radiations from the sun coupled with increased GHG from the atmosphere, causing global, temperature changes which results in variations in weather systems, melting of perma frost, sea rising and so on as observed by Lillesand, T. T. and Kiefer, R. W. [3] and Nelson, R. and Holben, B. [4].

The primary adverse effect of climate change is altering the complex web like system that allows life to thrive on the earth, thus affecting normalcy of cloud cover, rainfall availability, wind patterns, distribution of plants and animal species, leading to effects of floods, drought, famine, etc..

Kazimzumbwi Forest Reserve in Kisarawe district in Tanzania is endowed with a myriad of natural resources, including but not limited to forests, fauna and flora. These resources are susceptible to climate changes which put them to risk of extinction in the cause of sustaining livelihoods of people in the proximity of the forest reserve.

2. Problem Statement

As populations increase and national economies continue to move away from agriculture based systems, cities grow and spread i.e. urban sprawl. Urban sprawl often infringes upon viable agricultural land or production forest land neither of which can resist nor deflect the overwhelming urbanization momentum; as such, it results in degradation of the environment and deforestation [5], which particularly in developing countries is not well controlled due to limited knowledge and skills. This has an effect of disturbing the carbon dioxide equilibrium, resulting in polluting the environment. It is estimated that deforestation in Tanzania alone stood at 112,000

hectares per annum in 2009. This is an alarming rate which cannot be tolerated, as such, it has to be reversed to save the environment and the earth in general. However, reversing this trend requires quantitative data from which to design evidenced strategies that are designed to effectively curb or control it.

This paper is reporting on results of a study undertaken to quantify the extent of degradation that had taken place in Kazimzumbwi Forest Reserve in the period of 16 years effectively 1995 to 2011, for purpose of influencing policy intervention to control the situation.

3. Location of the Study Area

Kazimzumbwi Forest Reserve is situated in the Pugu Hills, approximately 20 km south-west of Dar es Salaam city in Tanzania; it is within 1 km of Pugu Forest Reserve (24 km²) as seen in Fig. 1. Together the two reserves form part of what was once a large forest block extending to within 10 km of Dar es Salaam. The TAZARA (Tanzania Zambia Railway) line goes through the reserve, through a nearby station Vigama on the western edge of the reserve.

4. Methodology

The study was based on multi-temporal satellite image analysis; Satellite images used were Landsat TM, all with cloud cover less than 10%. The images were pre-processed to remove radiometric and geometric errors prior to further processing [6]. The images were classified using ENVI software and post processing was done using ARCGIS.

5. Results and Analysis

Four land cover maps of the covering the forest reserve for the years 1995, 2000 2009 & 2011 were generated. Typical classes prevalent in the forest were found to be forest, shrubs, grass land and bare land. The results are as shown in Figs. 2-5.

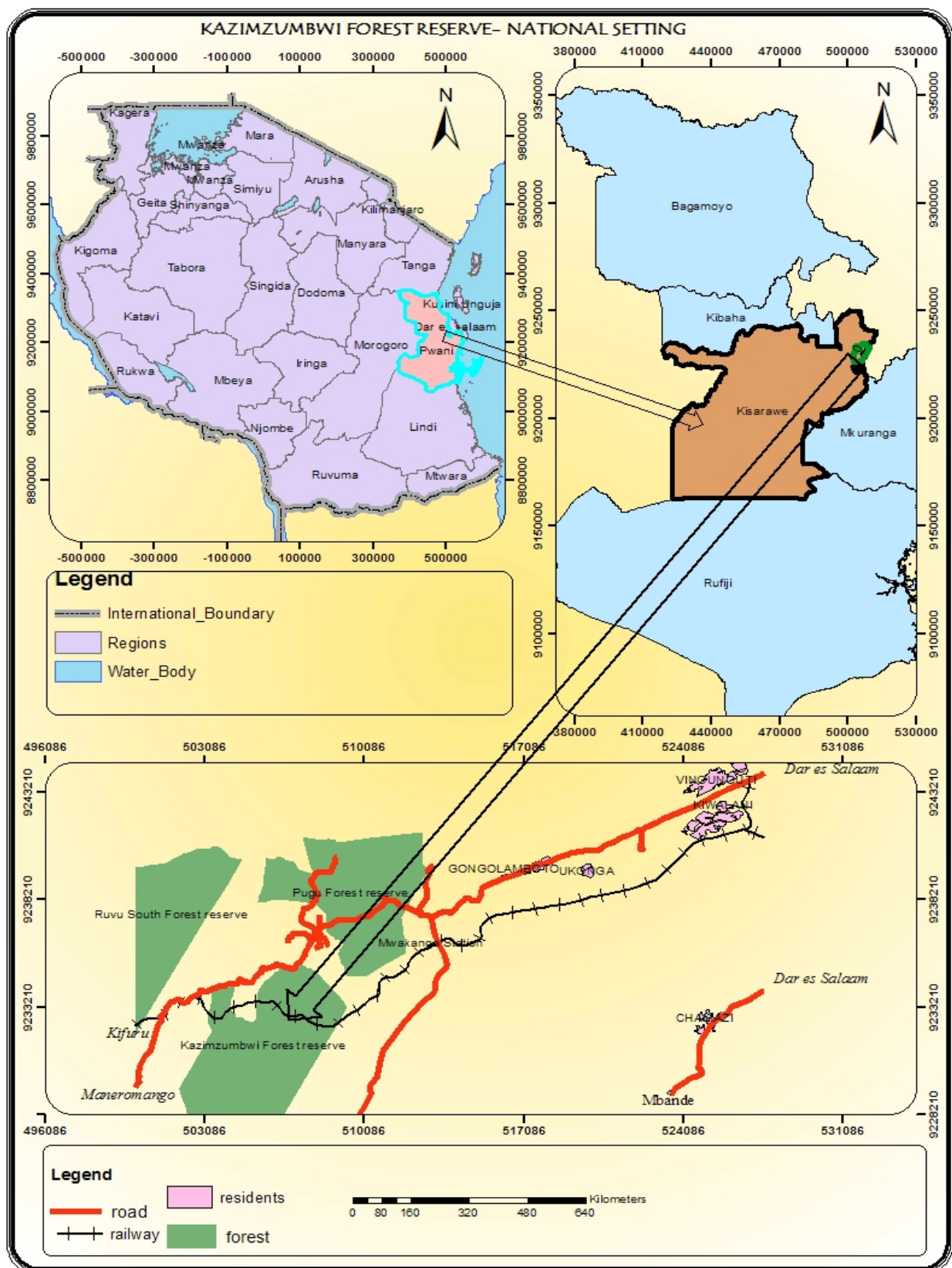


Fig. 1 Location sketch of Kazimzumbwi Forest Reserve.

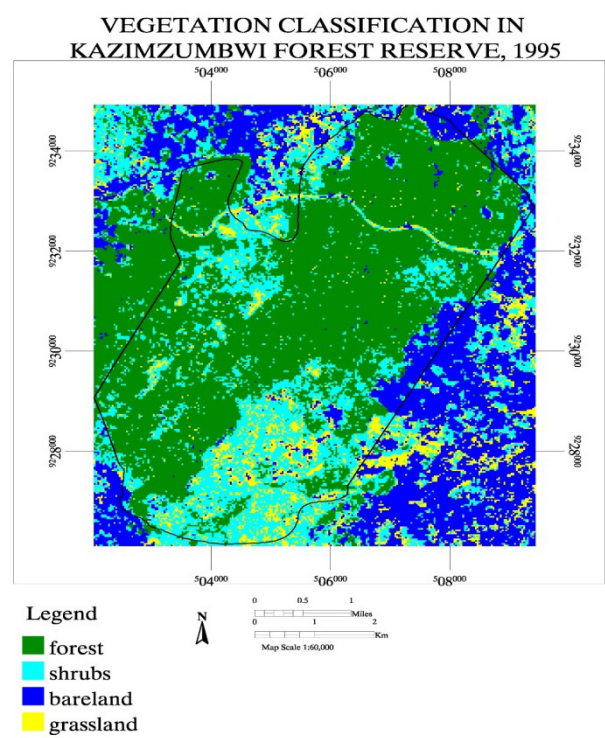


Fig. 2 Land cover map of Kazimzumbwi Forest Reserve in 1995.

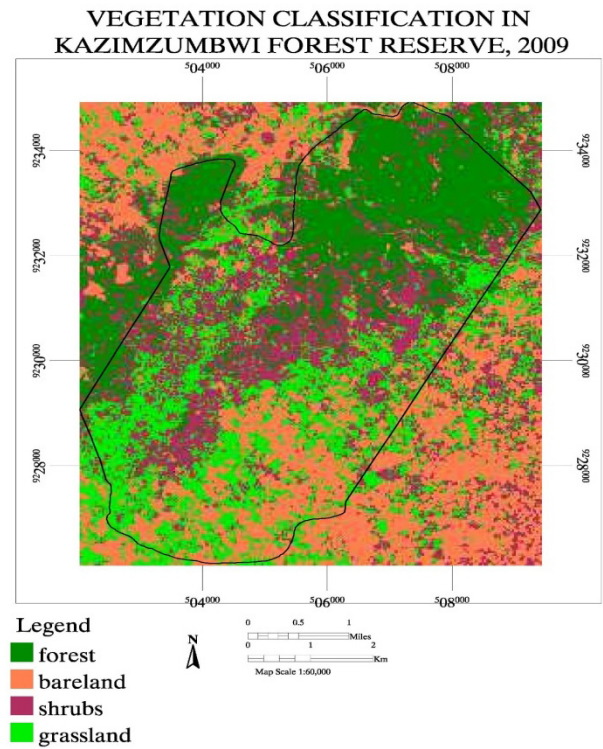


Fig. 4 Land cover of Kazimzumbwi Forest Reserve in 2009.

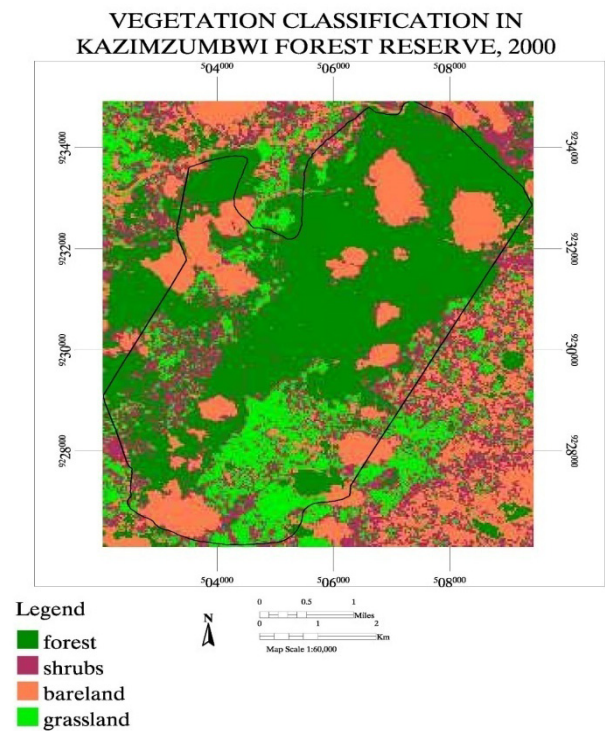


Fig. 3 Land cover map of Kazimzumbwi Forest Reserve in 2000.

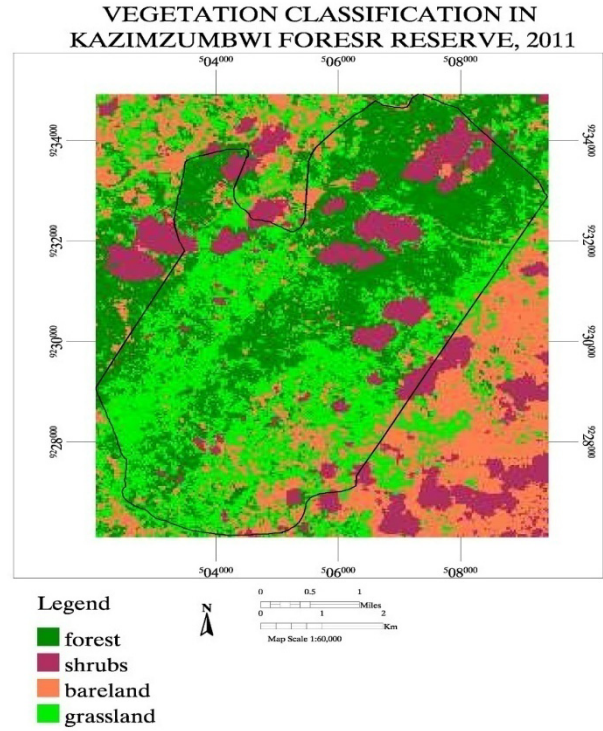


Fig. 5 Classified image results of 2011.

Table 1 Summary of accuracy assessment of classified images.

Classes	Forests (ha)	Shrubs (ha)	Bare land (ha)	Grass land (ha)	Overall accuracy %
1995	94.90	54.80	77.19	38.33	82.9
2000	398.43	50.63	67.15	87.91	82
2009	96.61	4.10	3.49	73.44	88.3

Table 2 Summary of land cover change from 1995 to 2011.

	Forests areas (ha)	Bare land areas (ha)	Shrubs areas (ha)	Grass land areas (ha)
2000	5,047.67	195.68	149.87	167.513
2009	2,927.65	246.56	50.96	234.478
2011	1,727.31	308.20	16.82	332.958
Average change (%)	- 42	+ 26	- 66	+ 42

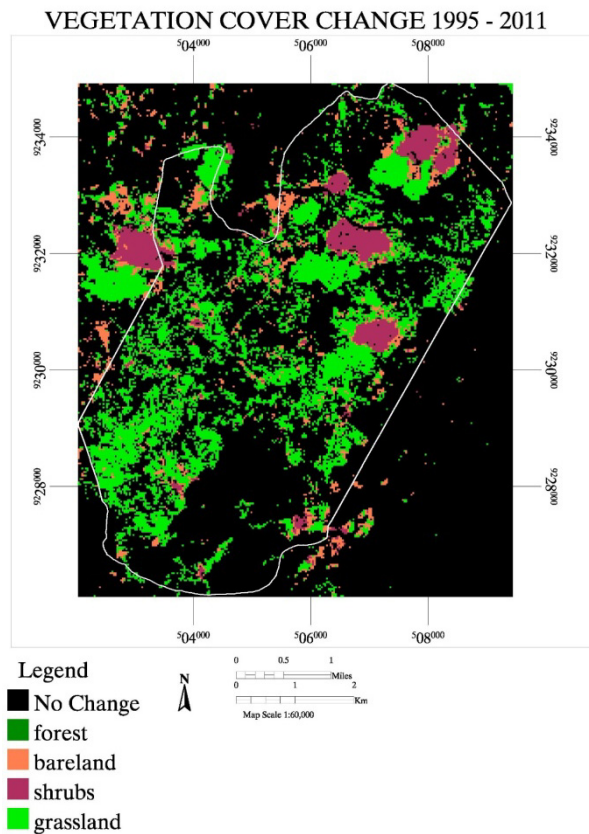


Fig. 6 Overall land cover change from 1995 to 2011.

5.1 Image Classification Accuracy Assessment

Satellite image classification accuracy was performed using the confusion matrix tool. The results are as summarized in Table 1.

5.2 Land Cover Change Detection

Change detection was performed by image differencing so as to assess the extent to which land cover of Kazimzumbwi Forest Reserve has changed from 1995 to 2011 (16 years) as done by Lu, D. [7] and Jensen, J. R. and Toll, D. L. [8]. The results are summarized on the Table 2 and Fig. 6.

6. Conclusions and Recommendations

In overall, the forests reserve have decreased by 42%; bare land has increased by 26% whereas shrubs decreased by 66% and grass land increased by 42% during the study period.

These results indicate a negative change in the forest resources, which is attributed to climate change effects, as forests are used to support livelihoods of most Dar es Salaam residents.

The Kazimzumbwi Forest Reserve was declared in 1936 and the government tolerated logging until the 1970s. After that time, human activities were not allowed in the forest reserve. During that time, the population around the area was small compared to the recent years. The rapid population increase around the area has lead to increasing demand in land for settlement and agriculture. Agricultural activities involves the cutting down of forests for clearance and trees for construction purposes as well as for firewood settlements, specifically in construction which involves the use of trees for wood for roofing also in social economic activities such as making of charcoal and firewood for cooking.

Allowing passage of a railway line across the forest reserve also contributed to degrading the environment, as the railway line attracted more population to the area with actions whose activities have always been detrimental to the environment.

Therefore, this decrease in dominant species in the reserve specifically forest and the shrubs is a testimony of environmental degradation and the decline of natural resources which collectively affect the entire ecosystem.

Controlling these activities is necessary so as to effectively mitigate the adverse effects of degradation and climate change for sustainable development.

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Modified Contingent Valuation Method for Agricultural Wastes between the Areas of Peloponnese and Thessaly in Greece

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Abstract: This paper focuses on investigating the tendency of farmers in the greater area of Peloponnese as well as those on the greater area of Thessaly to participate in a program of environmental agricultural waste management. The aim of the present study is to investigate the level of amount WTA (Willingness to Accept) against which the farmers would be willing to allow anyone to gather and carry away the leftovers of their farming exploitation. To serve the above goals, the agricultural leftovers are evaluated by the CVM (Contingent Valuation Method) as an environmental non-market economic commodity. The specimen response on utilization of the rejected biomass was satisfactory, since a good percentage of the interviewees are willing to contribute to this procedure for a minimal of remuneration, although investigations of this type are novel for Greek reality. From this investigation, it is perceived by the society the importance of alternative utilization of the rejected biomass. It is concluded that the minimum amount each interviewee is willing to accept as minimal remuneration and is affected by the way these biomass leftovers are managed, the age of the interviewees and the area in which they live. Those interviewees who use such biomass leftovers in alternative applications wish to be remunerated higher compared to those who relinquish such leftovers. The ordinal logistic model is listed in a broader category of generalized linear models for arrangement data.

Key words: WTA (Willingness to Accept), biomass, ordinal model, parametric approach, questionnaire, public good.

1. Introduction

The CVM (Contingent Valuation Method) is a survey-based technique, frequently used in experimental economics, especially useful for the valuation of non-market resources/goods/services, and cultural heritage objects (of aesthetic, historic, scientific or social value), such as conservation of monumental remains and preservation of the physical and anthropogenic environment [1, 2]. The basic partial techniques used in CVM are: (i) WTP (Willingness to Pay), which is the maximum monetary amount that an individual would pay to obtain/preserve a good and (ii) WTA (Willingness to Accept) compensation, which is the minimum monetary amount required to relinquish the good.

Therefore, WTP provides a purchase price, relevant for valuing the proposed gain of the good while WTA provides a selling price, relevant for valuing the proposed loss of the good. According to classic economic theory, a significant difference between WTP and WTA should not occur, on condition that there is: (i) no transaction cost; (ii) perfect information about goods/services and corresponding prices; (iii) no income effect; (iv) a market that engenders truthful revelation of preferences. Although these conditions were generally met in several economic experiments that used inexpensive market goods with readily available substitutes, the ratios WTA/WTP obtained were significantly greater than unity. This result was attributed to the fact that participants in these experiments lacked market experience [3]. CVM is the first technique of hypothetical experiments using a questionnaire applied to assess the economic value of

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public goods and services and is the predominant assessment technique in the scientific field of experimental economics.

The economic value of natural resources is often defined as the value of the goods and the services they offer. The environment economics have developed a series of methods for assessment of the monetary price of the environmental goods and services, which are based on investigation of the public preferences and reflect the practical need of translation of the monetary amount into management policies, in which the public concession and participation in the process of decision making are indispensable [4, 5].

The term biomass means the biodegradable products fraction, wastes and leftovers coming from agricultural, plants and animal substances inclusive, the forestall and the like industrial plant, as well as the biodegradable fraction of industrial wastes and urban effluents and sewage wastes [6-8].

2. Implementation

The results of the descriptive statistical analysis are compared among the answers of the interviewees in the mainland Greece (Thessaly) and on Peloponnese. The similarities and differences in the attitude of these two categories of rural population are outlined. It is observed that the interviewees in the previous year owned bigger areas of land (more km²) per cultivated item on Peloponnese compared to Thessaly. Also the interviewees stated that they had almost the same number of km² against the average km² owned by the farmers in Thessaly, on Peloponnese. Most of the interviewees in Thessaly utilize the crop leftovers in other applications but on Peloponnese gather it for fuel at home. It is worth noting that management of the rejected biomass does not differ among the areas of Thessaly and Peloponnese in Greece [9].

On the contrary, however, it is noticed that the minimum compensation amount each interviewee asks in order they may be in a position to gather and carry away the leftovers differs among the areas. More

specifically on Peloponnese, the farmers ask for higher remuneration compared to farmers in the Thessaly area. However, the willingness shown by the farmers for participation in gathering the crops without any extra remuneration does not differ among the areas. As regards the income of each interviewee farmer against that of inhabitants in other areas of similar agricultural exploitation, it does not differ between the two area categories, as the results show. Additionally, it is noticed that the percentage of the interviewees' income originating in farming is bigger in Thessaly compared to that on Peloponnese. In order the amount WTA is correlated with the rest of the parameters of that example, the model 'ordinal regression' is applied, given that the dependent variable (WTA) is scaled and the independent variables are discrete (nominal or scaled) [10, 11].

3. Statistical Data and Results

It is shown that the minimum amount each interviewee is willing to accept as minimal remuneration, is affected by the way these biomass leftovers are managed, the age of the interviewees and the area in which they live. Those interviewees who use such biomass leftovers in alternative applications wish to be remunerated higher compared to those who relinquish such leftovers [12-15].

The interviewees aged 15 to 25 years wish to be remunerated with smaller amounts compared to those aged 56 up (p -value = 0.045 < 0.05). Further, it is noticed that the farmers aged 26 to 40 years wish to be remunerated with higher amounts compared to those of 56 years up (p -value = 0.018 < 0.05). Finally, the interviewees in the Thessaly area wish to be remunerated with smaller amounts compared to those on the islands of Peloponnese.

The ordinal logistic model is listed in a broader category of generalized linear models for arrangement data. The model is based on the assumption that a latent continuous outcome variable exists.

The specimen numerator determines the location of

the model while the denominator determines the scale. The scaled components are the cause of differences in the variable of different values of the predictor variables.

The question formulates the WTA of the interviewee that is their wish for remuneration in order to allow someone to gather and take away the leftovers of the agricultural exploitation. It is impressive that the majority of the interviewees, i.e. 71.7% of the specimen, answered that they would relinquish their farming leftovers without asking for any monetary remuneration. Out of the remaining 28.3% of the specimen, 11.7% answered that they would ask for 1-5 euro to relinquish the farming leftovers in each cultivated km² on a yearly basis. Similarly, another 11.7% of the specimen answered that they would ask for 6-10 euro for the same reason. Finally, one person in each category (1.67% of the specimen), answered that the remuneration he would ask to relinquish his farming leftovers would be 11-15 euro in the first instance, 16-20 euro in the second instance and 21 euro up in the last instance.

It is observed that in the first category, that is the one of those stating that they do not ask for any remuneration to relinquish their farming leftovers, 58.1% of the specimen would participate without any recompense in the entire process, while 41.8% would not participate without recompense.

In the second category, that is the one of those wishing to collect monetary remuneration to relinquish their farming leftovers, 47% of the specimen answered that they would participate in the relevant procedure, contrary to the 52.9% of the interviewees who stated that they would not participate.

In the first category, i.e. those who stated that they do not wish any remuneration to relinquish their farming leftovers, 58.1% of the specimen would participate in the whole procedure without recompense while 41.8% would not participate without recompense.

In the second category, i.e. those wishing to collect monetary remuneration to relinquish their farming leftovers, 47% of the specimen answered that they would participate in the relevant procedure, but 52.9% of the interviewees stated that they would not participate.

Out of the first category which concerns those not wishing remuneration to relinquish their farming leftovers, 26% of the specimen stated that they abandon their farming leftovers in the field. An equal percentage (26%) states that they burn the leftovers in the field. Only 2.3% gather the leftovers as fuel at home while, finally, the majority that totals 45.2% mention utilization.

Out of the second category, which concerns those wishing remuneration to relinquish their farming leftovers, 26% of the specimen stated that they abandon the leftovers of their farming exploitation in the field.

Out of the first category, i.e. those stating that they do not wish any remuneration to relinquish their farming leftovers, 18.6% of the specimen report an income smaller than the average of the farmers in the area who are involved in similar farming exploitation, 67.4% of the specimen report an income approximately equal to the average and finally only 13.9% of the interviewees report an income bigger than the average in the area.

Out of the second category, that is the one wishing to collect monetary remuneration to relinquish their farming leftovers, 23.5% of the specimen report an income smaller than the average of the farmers in the area with similar farming exploitation, 47% of the specimen report an income approximately equal to that of the average and finally only 29.41% of the interviewee report an income bigger than the average in the area.

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (1)$$

In Eq. (1), N is the number of observations; y is the dependent variable; $\bar{y}$ is the mean of the y values; and $\hat{y}$ is the value predicted by the model. R^2 is the determination coefficient that ranges from 0 to 1. According to the Ephron's R^2 (Eq. (2)):

$$R^2 = 1 - \frac{\sum_{i=1}^N (y_i - \hat{\pi}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (2)$$

where $\hat{\pi}$ = model predicted probabilities, the dependent variable in a logistic regression is not continuous while the predicted value (a probability) is. The log likelihood of the intercept model (Eq. (3)) is:

$$R^2 = 1 - \frac{\ln \hat{L}(M_{Full})}{\ln \hat{L}(M_{Intercept})} \quad (3)$$

$$2 \ln [L(M_{Intercept}) / L(M_{Full})] \quad (4)$$

In Eq. (4), M_{Full} is the model with predictors; $M_{Intercept}$ is the model without predictors; and $\hat{L}$ is the estimated likelihood. A likelihood falls between 0 and 1, so the log of likelihood is less than, or equal to zero. If a model has a very low likelihood, then the log of the likelihood will have a larger magnitude than the log of a more likely model. The R^2 as a transformation of that statistic analysis used to determine the convergence of a logistic regression (Eq.(5)):

$$R^2 = 1 - \left\{ \frac{L(M_{Intercept})}{L(M_{Full})} \right\}^{\frac{2}{N}} \quad (5)$$

Note that pseudo- R^2 has a maximum value that is not 1; if the full model predicts the outcome perfectly and has a likelihood of 1, then Eqs. (6, 7):

$$1 - L(M_{Intercept})^{\frac{2}{N}} < 1 \quad (6)$$

$$R^2 = \frac{1 - \left\{ \frac{L(M_{Intercept})}{L(M_{Full})} \right\}^{\frac{2}{N}}}{1 - L(M_{Intercept})^{\frac{2}{N}}} \quad (7)$$

It should be noted that adjustment of the model is considered good by the first coefficient is 0.656 and

the second coefficient is 0.683.

4. Conclusion

The external effects are observed when supply or demand imposes costs or confers a benefit to others. More specifically, the external effect is the impact of the behaviour of a producer or consumer well-being on another, which is not reflected in market transactions.

The economic evaluation of research aimed at improving overall social welfare. As an initial test for social welfare, the criterion used Pareto, under which a fully competitive market, an action or policy is socially desirable if it improves the position of all the individuals composing the society or at least some (weak criterion Pareto), but difficult position of any other (a strong criterion Pareto). Some benefits from the research are as: He offered a variety of options that allow the construction of statistical models capable. The number of interviews and the survey costs are lower compared to those required for investigations manifested preferences. However, this indicated drawbacks, such as the fact that: there was a bias due to discrepancies between stated intentions and actual behaviour of interviewees.

The specimen response on utilization of the rejected biomass was satisfactory, since a good percentage of the interviewees are willing to contribute to this procedure for a minimal of remuneration, although investigations of this type are novel for Greek reality. From this investigation, it is perceived by the society the importance of alternative utilization of the rejected biomass.

It is impressive that the majority of the interviewees, i.e. 43 persons who represent 71.7% of the specimen answered that they would allow their gathering and carrying away of their farming leftovers without asking for any monetary remuneration. Further, encouraging are the results concerning the willingness to participate in the gathering since the majority of the interviewees, i.e. 55% of the specimen, stated that

they would participate in the gathering of the leftovers without any remuneration.

With regard to the amount WTA (dependent variable) of the logit model, it is concluded that it is affected by the wish for remuneration (independent variable) at the level of importance 5% (p -value = 0.011). It is also concluded that the amount of WTA is affected by the km^2 each farmer owns compared to other farmers at the level of importance 10% (p -value = 0.065).

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Mining Contribution to Municipalities Development

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Abstract: Mining activity in Brazil has significantly contributed to the country development. However, this contribution is not always fully noticed by society. This study aims to bring more evidence to this mining activity contribution, based on highly regarded development indicators, such as the HDI (Human Development Index), created by the UNDP (United Nations Development Programme). The HDI was traditionally designed as an instrument to evaluate the degree of countries development and was subsequently deployed to states and municipalities (IDHM (Municipal Human Development Index) for Brazilian municipalities). In addition to IDHM released by the UNDP, FIRJAN (Federation of the Industries of the State of Rio de Janeiro) developed its own IFDM (FIRJAN Municipal Development Index). The statistical analysis shows that the average of the municipalities with mining activities has superior development indices than those with non-mining activities, especially in the two major mining states: Minas Gerais and Pará.

Key words: Mineral activity, human development, IDHM (Municipal Human Development Index), IFDM (FIRJAN Municipal Development Index).

1. Introduction

Brazil has one of the world's largest reserves of metallic and non-metallic minerals [1]. Brazil's largest mining companies are also among the world's largest mining companies, with the major part of their production destined for export. Mining industry has significantly contributed, directly and indirectly, to Brazil's economy. According to the IBRAM (Brazilian Mining Association), the whole extractives sector (including oil and gas) accounted for 3% of the GDP (Gross Domestic Product) of the country [2]. In foreign trade, mining industry contributed more than US\$ 34 billion in mineral exports in 2014 and had also provided a multiplier effect of up to 13 indirect or induced jobs; that is, almost 2.7 million workers involved in some way with the mining activity [1]. Mineral extraction accounts for US\$ 727 million in Brazilian tax collection royalties in the year 2014 [3].

This research aims to quantify the contribution of the

mining activity in the development of the municipalities that have this type of activity in its territory, using the HDI (Human Development Index) as a measure. Created for the UNDP (United Nations Development Programme), the HDI was traditionally designed to evaluate the degree of countries development, consolidating since the 1990s as the best-known indicator for such purposes [4, 5].

Subsequently, the HDI has been adapted to states and municipalities, giving rise to the IDHM (Municipal Human Development Index), published by the UNDP [5, 6], FIRJAN (Federation of the Industries of the State of Rio de Janeiro) [7] and IFDM (FIRJAN Municipal Development Index). IDHM is calculated from data on income, longevity and education census conducted every ten years by the Brazilian Institute of Geography and Statistics [6]. On the other hand, IFDM is updated through government official employment, income, health and education data, which provides an annual disclosure of this indicator [7]. The two indices range from 0 to 1. The closer to 1, the higher human development is.

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The HDI metric indicates that Norway and Australia are two of the most developed countries of the world and both have a significant share of the mining activity in GDP. Thus, authors use the IFDM and IDHM to verify through statistical evidence if the municipalities that have mining activity have a development index superior to the others. Here, it is considered that the mining municipalities are those which have collected the CFEM (Financial Compensation for Exploration of Mineral Resources) in the last 6 years (2010-2015) [3].

The paper is organized in two parts. The first used hypothesis test with a 5% significance level to verify if the municipalities with mining activity (in this paper referred to as “mining cities”) have development indices superior to non-mining municipalities. In the second part, it was demonstrated through histograms, the percentiles where are located the main mining cities of the two major Brazilian mining states (Pará and Minas Gerais), accounting for 80% of CFEM collected over the past 6 years (2010-2015).

1.1 Theoretical Framework

One of the major concerns of the international organizations is the progress of the human being in terms of development. This trajectory has been monitored and evaluated by several government institutions, social scientists and academics, with the objective to subsidize the decision and orientation of the development of corporate actions and public projects. Several indicators can be used to evaluate these trends, but some indicators have become frequent in the evaluation of these interventions [8-11]. In this regard, the recommendations of the United Nations Commission on Sustainable Development have become popularly known among policymakers, who have strongly argued that indicators are needed to monitor progress towards sustainable development in order to assist decision-makers at all levels. In addition, the commonly used economic welfare indicators should also be considered as social, environmental and

institutional indicators to achieve a broader and more complete picture of the social development. From this wide approach, social scientists have used HDI as a standard measure to analyze the progress of human development at the municipal level and also to run comparative analysis [8, 9]. In parallel, alternative indicators have also emerged to evaluate the human progress variables in a temporal scale. For example, FIRJAN is one example of the human progress indicator [11].

The most widely used indicator for assessing a country's performance is the HDI. According to The Economic Times [12], “HDI is a statistical tool used to assess a country's overall achievement in its social and economic dimensions. The social and economic dimensions of a country are based on people's health, their level of education and their standard of living.” According to UNDP [13], “the goal of creating the HDI was to offer a counterpoint to another widely used indicator, the GDP per capita, which considers only the economic dimension of the development.” Created by Mahbub ul Haq with the collaboration of the Indian economist Sen, A. [4], winner of the 1998 Nobel Prize in economics, “the HDI is intended as a general and synthetic measure that, although broadening the perspective on human development does not cover nor exhaust all aspects of development.”

To measure the development of municipalities, UNDP proposed an adaptation of HDI to generate the IDHM. This organization defines it as “a measure made up of indicators of three dimensions of human development: longevity, education and income” [6]. The index ranges from 0 to 1, like the original HDI. The Brazilian IDHM follows the same three dimensions of the global HDI—longevity, education and income, but it goes farther and adapts the global methodology to the Brazilian context and the availability of national indicators. Although they measure the same phenomena, the indicators taken into account in IDHM are more adequate to evaluate the development of Brazilian municipalities [6].

The IDHM update is based in the Brazilian Institute of Geography and Statistics census data, thus, its last update was in 2010. Considering this, FIRJAN developed the IFDM, an indicator with a similar method of HDI, but which allows an annual update according to this federation. IFDM is a study from the FIRJAN system that annually accompanies the socioeconomic development of more than 5 thousand Brazilian municipalities in three basic criteria: employment & income, education and health. Created in 2008, it is exclusively based on official public statistics made available by the Ministries of Labor, Education and Health [7].

2. Material

This research aims to test whether there are significant differences in the mean IDHM and IFDM indicators for mining cities comparatively to non-mining ones in Brazil with a 5% level of significance, that is, if the mining cities have better performance in these indicators in average when compared with other municipalities.

The material used in this research refers to the registration of IDHM (2010) and IFDM (2013) of municipalities with mineral activity *versus* municipalities that do not have mining activity. The importance of the participation of the mining activity in municipal revenues is an indicative of the mining participation degree in that municipality. The groups were divided into centiles (10th centile, 5th centile, 1st centile and all municipalities that have collected CFEM for the last six years) gathered by revenues of CFEM in relation to the total revenue collected by the municipality, on average, in the period from 2010 to 2015. Thus, the groups consider all mining municipalities, which have relevance above 1%, 5% and 10% of CFEM compared to the total revenue of these mining cities, as informed on the balance sheets disclosed in the STN (National Treasury Secretariat) website [14].

In order to test whether the means of these indicators

are different or not, the t-test was developed for independent samples, which requires the normality of the data distribution and homogeneity of variances. Thus, data were submitted to normality test using Kolmogorov-Smirnov and Levene tests to assess whether the variances are homogeneous. In the case of evidence to reject the null hypothesis, it is concluded that the indicators fit the non-parametric Mann-Whitey statistic, which is used to test the equality of means when the assumptions of normality are violated.

3. Results and Discussion

3.1 Results and Statistical Tests

To test the hypothesis that municipalities with mineral activity have development indices superior to other municipalities, the averages of the two development indices covered in this research (IFDM and IDHM) were compared in four mining presence levels according to the collection of CFEM of last six years by revenue. In all comparisons, for IFDM and IDHM, the mining cities averages were higher than non-mining. Moreover, there was an increase in development rates in both indicators, as it increases the participation of CFEM in municipalities' revenue, as shown in Tables 1 and 2.

To confirm the statistical significance of the superiority of human development average of mining municipalities, the normality of the data were tested to see which statistical test is more appropriate for this data profile through its probability value (p-value). Tables 3 and 4 confirm that data are not normal and Tables 5 and 6 show that the averages are not homogeneous.

As the normality of the data was not confirmed, the nonparametric Mann-Whitey was used, which confirmed that indeed the mining cities have higher development indices, measured by IDHM and IFDM at a 5% significance level, in the four levels of mining influence, as shown in Table 7 through the p-value.

Table 1 Municipality IDHM average.

Centile-levels of influence of collected CFEM	Non-mining	Mining
All	0.6443	0.6772
1st centil	0.6584	0.6803
5th centil	0.6590	0.6824
10th centil	0.6590	0.7156

Table 2 Municipality IFDM average.

Centile-levels of influence of collected CFEM	Non-mining	Mining
All	0.6319	0.6744
1st centil	0.6502	0.6863
5th centil	0.6508	0.6878
10th centil	0.6508	0.7281

Table 3 Kolmogorov-Smirnov test (p-value) applied to IDHM.

Centile-levels of influence of collected CFEM	Non-mining	Mining
All	0.0000	0.0000
1st centil	0.0000	0.0180
5th centil	0.0000	0.1660
10th centil	0.0000	0.2000

Table 4 Kolmogorov-Smirnov test (p-value) applied to IFDM.

Centile-levels of influence of collected CFEM	Non-mining	Mining
All	0.0000	0.0000
1st centil	0.0000	0.0130
5th centil	0.0000	0.0300
10th centil	0.0000	0.0690

Table 5 Variance test (p-value) applied to IDHM.

Centile-levels of influence of collected CFEM	Brazilian municipalities
All	0.0000
1st centil	0.0000
5th centil	0.0810
10th centil	0.0010

Table 6 Variance test (p-value) applied to IFDM.

Centile-levels of influence of collected CFEM	Brazilian municipalities
All	0.2300
1st centil	0.0000
5th centil	0.5370
10th centil	0.1650

Table 7 Mann-Whitey test (p-value).

Centile-levels of influence of collected CFEM	Brazilian municipalities
All	0.0000
1st centil	0.0000
5th centil	0.0270
10th centil	0.0000

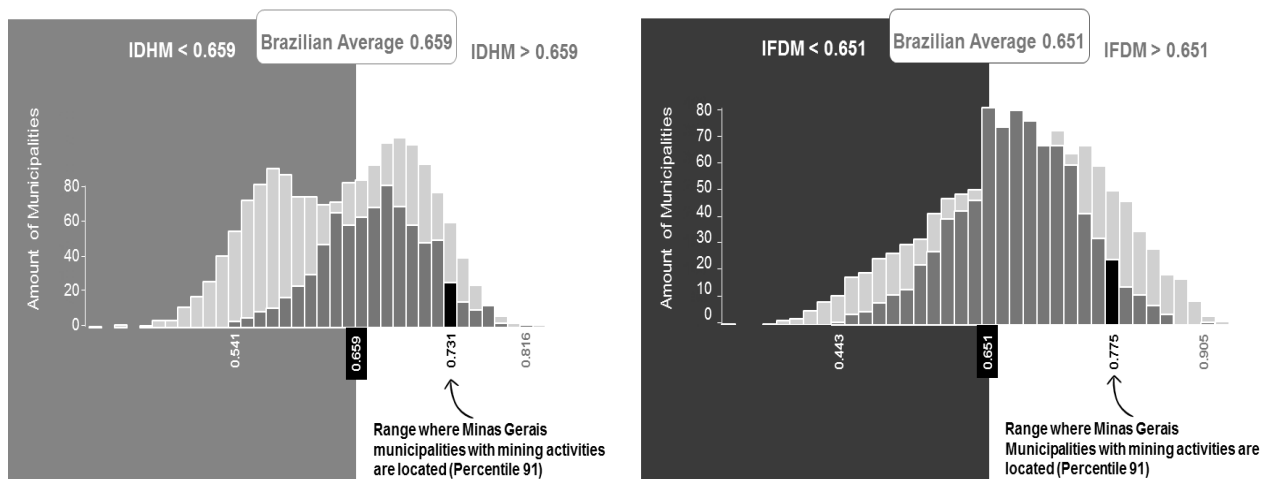


Fig. 1 Distribution of Minas Gerais municipalities by IDHM and IFDM (mining municipalities are represented by dark gray bars) [3, 6, 7, 14].

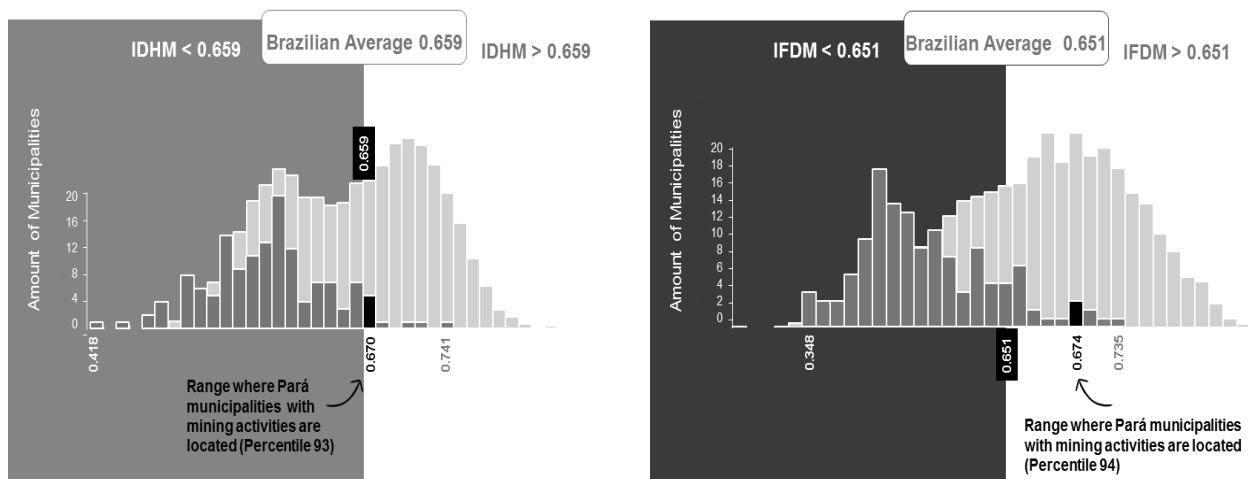


Fig. 2 Distribution of Pará municipalities by IDHM and IFDM (mining municipalities are represented by dark gray bars) [3, 6, 7, 14].

3.2 Positioning of the Main Mining Cities in Minas Gerais and Pará

Both states of Minas Gerais and Pará together account for 80% of the Brazilian CFEM collected in the past six years (2010-2015). It can be seen that the mining municipalities occupy a prominent position in tax collection in these states. The most important mining municipalities (91% of revenues) in Minas Gerais are positioned in the percentile 91 in IDHM and 91 in IFDM distribution of mining municipalities. In Pará, the most important mining cities (90% of revenues) are positioned in the percentiles 93 in IDHM and 94 in IFDM distribution of Pará

municipalities (in both cases represented by few municipalities above Brazilian average). These results are shown in the histograms of Figs. 1 and 2.

4. Conclusions

This study analyzed the contribution of mining activities to the development of Brazilian municipalities where it is present. It was used 2010 IDHM and 2013 IFDM development indicators, applied in municipalities with mining activity identified by the collection of CFEM as published at DNPM (National Department of Mining Production) site [3].

The hypothesis that mining municipalities have higher rates of development than the non-mining ones was tested in four levels of mining influence, as measured by the volume of CEFEM collection, represented in relation to their total revenue. The result of the study showed that mining cities are more developed than non-mining ones in all four levels of influence, considering IDHM and IFDM, to a statistical level of significance of 5%. It was also found that the averages on both indicators increase as the level of mining influence increases.

The increase in human development indicators for mining cities is more evident in the states of Minas Gerais and Pará. These two states are responsible for 80% of Brazilian CFEM collected over the last six years (2010-2015), where the main mining cities in both states are responsible for 90% of the tax collection over those years. In addition to that, they are located above the 90th percentile of the distribution of the cities from these two states.

It is noteworthy that the factors analyzed in this study only explain the part related to the influence of mining activity. There are other variables, such as public policies and administration, culture and history of the city, among other factors, which may also influence human development index.

Finally, it is important to pay attention to the recommendations of expansion of the wealth concept proposed by Stiglitz, J. E., et al. [15], whose consequences change the concept of human development indicators.

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Journal of Environmental Science and Engineering B
Volume 6, Number 8, August 2017

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